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Jerusalem- Palestine
1427/ 2006

TO

MY PARENTES,

MY WIFE & MY FAMILY

Declaration

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institute.

Signed:……..

Talib Musa Ahmad Ihmied

Date:

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Abstract

Chromium exists mainly in two oxidation states III and VI. The higher oxidation state is known for its severe toxicity to humans and environment. According to International environmental quality standards; the maximum allowed level for Cr(VI) should not exceed 0.05 ppm in drinking water [(2)]. The lower oxidation state is less harmful and is allowed to have a value of 5 ppm. Standard analytical procedure using ICP-AES or atomic absorption spectrometry do not allow for the separate detection of these ions and hence invoke expensive remediation processes. In previous work batch reactor process identified wool as a good absorber of Cr(VI) at low pH. In this work, sand and wool are utilized for continuous removal of chromium from aqueous solution. The results indicate that sand at low pH absorbs Cr(III) efficiently and selectively with more than 99% removal and hence leaving Cr(VI) in solution. On the other hand, wool is found to be more selective towards Cr(VI). Two sequential columns are designed and optimized for speciation and removal of chromium. The first was made of sand and the other is from wool. Flow rates, pH, contact time, column depth, initial metal concentration, adsorbent size, and wool dyeing with AVN are found to affect the efficiency of speciation and removal. The results showed that the initial concentration of chromium has a clear effect on the percent removal of chromium. The experimental adsorption data on wool using continuous flow method could be explained in terms of two forms of actions occurring simultaneously. The first is reversible form (desorption) and the other is irreversible form (adsorption). The desorption is found dependent on temperature and contact time between the mobile phase, Cr(VI) buffered solution, and wool. The experimental results points out that continuous method is efficient, fast and low cost for the speciation of Cr(III) and Cr(VI) and could be applied at large for industrial wastewater treatment.

A freshwater plant, duckweed which is uniquely suitable for aquatic toxicity tests is utilized to study the accumulation of chromium at different temperature. It was found that the percentage removal is small. And the duckweed is dead because the accumulation of Cr(VI) [(128)].

الملخص

عنصر الكروم موجود على عدة أشكال تأكسد في الطبيعة ومن أهم هذه الأشكال الكروم الثلاثي والسداسي التأكسد. الكروم السداسي معروف بتأثيره السام على البشر والطبيعة واعتمادا على معايير الجودة العالمية للبيئة يجب أن لا يزيد تركيز هذا الايون على 0.05 ملغم/لتر في المياه المستخدمة للشرب. أما الكروم الثلاثي التأكسد فهو اقل ضررا والحد المسموح به في المياه هو 5 ملغم / لتر. حيث يستخدم جهازي انبعاث الطيف الذري (ICP-ASE) و الامتصاص الذري (AAS) في الكشف عن عنصر الكروم ولكن لا تستطيع هذه الأجهزة الكشف عن هذه الايونات وفصلهما يتطلب تكاليف عالية.

في العمل السابق وجد أن الصوف الطبيعي ماص جيدا للكروم السداسي على درجات حموضة منخفضة وذلك باستخدام عملية النقع (Batch Technique). أما في هذا العمل فاستخدمنا الرمل والصوف الطبيعي لإزالة الكروم من المياه العادمة باستخدام التدفق المستمر (Continuous Flow Technique) . حيث وجدنا أن الرمل يمتص الكروم الثلاثي وبشكل جيد وانتقائي على درجات حموضة منخفضة، وقد وصلت نسبة الإزالة لهذا الايون حوالي ٩٩% تاركا الكروم السداسي في المحلول أما الصوف فوجدنا انه يمتص الكروم السداسي وبشكل انتقائي على درجة حموضة ١. وبناءا عليه يمكن فصل الكروم السداسي عن الثلاثي باستخدام أنبوبين متسلسلين احدهما يوجد بداخله رمل والأخر صوف.

صممت التجارب لدراسة تأثير عوامل مختلفة على إزالة الكروم وهي سرعة التدفق، درجة الحموضة، زمن التلامس، ارتفاع الصوف في الأنبوب، تركيز الكروم الأولي، حجم مادة الامتصاص، وصباغة الصوف. حيث أظهرت النتائج أن تركيز الكروم الأولي له تأثير واضح على نسبة الإزالة. حيث وجدنا أن هناك امتصاص (adsorption) على الصوف وأيضا ايونات من الكروم تعود مرة أخرى إلى المحلول (desorption) . ووجد أن (desorption) يعتمد على درجة الحرارة وزمن ترك الأنبوب. حيث تشير النتائج بان طريقة (Continuous Flow Technique) ذات كلفة منخفضة وسريعة ويمكن أن تطبق بشكل أوسع واكبر في معالجة المياه الصناعية.

كما استخدمنا أيضا العدس المائي (Duckweed) لإزالة الكروم على درجات حرارة مختلفة ولكن العدس المائي مات بسبب تراكم تركيز الكروم في العدس المائي، حيث وجد أن نسبة الإزالة كانت قليلة.

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List of Abbreviations

EPA	Environmental Protection Agency
Cr(III)	Trivalent chromium ion
Cr(VI)	Hexavalent chromium ion
ppm	Parts per million (mg/l)
IRN77 and SKN1	Cation exchange resins
ICP- AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
AAS	Atomic Absorption Spectrometry
AVN	Acid alizarin Violet N
K_c	The equilibrium constant
$\Delta H°$:	The enthalpy change
$\Delta G°$	The free energy change
$\Delta S°$	The entropy
T	The temperature in Kelvin
R	The gas constant = 8.3314 J/ K mol
M_i	The initial mass of chromium
M_L	The mass of chromium leached
C_c	The concentration of Cr(VI) in control beaker (ppm)
C_d	The concentration of Cr(VI) in duckweed beaker (ppm)
pH_i	pH of influent solution
pH_f	pH of effluent solution
O.N	Over night

I

INTRODUCTION

I.1. Chromium environmental impact

Chromium (Cr) is a metallic element which is listed by the Environmental Protection Agency (EPA) as one of 129 priority pollutants [1, 2]. Chromium is found in all phases of the environment, including air, water and soil and it occurs in several oxidation states ranging from Cr^{2+} to Cr^{6+}, with the trivalent and hexavalent states being the most stable and common forms [3, 4]. Therefore, it can be both beneficial and toxic to animals and humans depending on its oxidation state and concentration [5-8]. These forms display different chemical, biological, as well as environmental properties. The trivalent state is insoluble at higher pH levels and is fairly easy to remove from water. The hexavalent state is very soluble over a broad pH range and considered to be the most toxic form of chrome. Cr(III) is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals [9, 10]. In contrast, Cr(VI) is highly toxic carcinogen and may cause death to animals and humans if ingested in large doses [11, 12]. Hexavalent chromium compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of soil, sediment, surface and ground waters [13, 14]).

According to international standards wastewater effluents must not contain more than 0.05 ppm Cr(VI) and 5.0 ppm Cr(III) [2, 6]. Most of the Cr(VI) found in nature as a result of domestic and industrial emissions. Interaction of Cr(VI) molecules with organic compounds can be reduced to a comparatively less toxic trivalent form. Cr(III) forms stable complex with negatively charged inorganic and organic compounds, Remediation of Cr(VI) contaminated soil and groundwater has focused on reduction of Cr(VI) to Cr(III) [13, 14]. Recently, direct metabolic reduction of Cr(VI) has received significant interest among researchers since the technology appears to be cost effective and does not produce secondary wastes. A range of bacteria are capable of using Cr(VI) as a terminal electron acceptor in their metabolic process and reduce Cr(VI) to insoluble and less toxic Cr(III), theoretically resulting in the immobilization of chromium in the subsurface [15-20].

Chromium is commonly used in various industries because of the characteristics of the metal and its compounds, resulting in large quantities of this element being discharged into the environment [21, 22]. These industries are metallurgical, electroplating, production of paints and pigments, tanning, and wood preservation [23, 24]. The tanning industry is an especially large contributor of chromium pollution to water resources. Leaching and seepage of Cr(VI) from the soils into the groundwater posses a considerable health hazard [25].

I.2. Treatment technologies

In the different compartments of the environment, chromium occurs mainly in the oxidation states (III) and (VI). These compounds have different solubilities and toxicities. While Cr(III) is an essential trace element and important for the glucose tolerance factor, Cr(VI) is highly carcinogenic and mutagenic [7, 8]. Therefore, it is necessary for risk assessment, not only to determine the total chromium in the different environmental compartments, but also to determine chromium in its different oxidation states. There are various treatment techniques for recovering or removing chromium from wastewater chemical reduction [26-30] and precipitation [14, 31], ion exchange [32-37], membrane technologies [38, 39] and adsorption [40-54] by several types of adsorbents; activated carbon [55-58], fly ash [59] and bone charcoal [60, 61] are examples of these adsorbents. In many cases,

the environmentally most compatible and cost effective solution comprises a combination of two or more of these processes. Most of these methods suffer from some drawback such as high capital and operational costs. Some of these methods are introduced below:

I.2.1. Reduction

Reduction is the gain of electrons, thereby decreasing the valence of an ion to a more negative state. Cr(VI) can be reduced to trivalent chromium, which is much less soluble and is an essential trace nutrient. The mechanisms of Cr(VI) reduction are technologically and biologically important because they convert a toxic, mobile element into a less toxic, immobile form. It is essential to understand these processes since reduction products, as well as their stability, are dependent on specific redox mechanisms and the environment. The most chemical reactants used for converting Cr(VI) to Cr(III) are, ferrous compounds, hydrogen peroxide (H_2O_2), reductive sulfur compounds, hydrazine (H_2NNH_2), hydroxylamine (H_2N-OH) and formaldehyde (HCHO). Most of these reducing agents are applied in aqueous acidic solution except for Fe(II), hydrazine, and hydroxylamine [62-64]. Bioremediation processes have also been found to transform Cr(VI) to Cr(III) [10, 13].

Chemical method and electrochemical are two methods used to remove Cr(VI) from industrial wastewater and both are based on the same general reaction:

$$3Fe(II)_{(aq)} + Cr(VI)_{(aq)} \longrightarrow 3Fe(III)_{(aq)} + Cr(III)_{(aq)}$$

But in the chemical method $Fe(II)_{(aq)}$ is supplied by dissolving $FeSO_4.7(H_2O)_{(s)}$ into the wastewater, while in the electrochemical process $Fe(II)_{(aq)}$ ions are formed directly in solution by anodic dissolution of steel electrode. Iron(II), an element common in soil and sediments under anaerobic conditions, can serve as a reducing agent for Cr(VI) and it is the most important reductants of Cr(VI) [66-69]. Zero-valent iron (Fe(0)) has been used to reduce Cr(VI) in groundwater, especially with reactive permeable barrier walls and nanoscale particles.[63] This reduction with Fe(0), and subsequent precipitation of Cr(III) hydroxides occurs through the following reaction:

$$3/2Fe(0)_{(s)} + CrO^{-2}_{4(aq)} + 5H^{+}_{(aq)} \longrightarrow 3/2Fe^{+2}_{(aq)} + Cr(OH)_{3(s)} + H_2O_{(l)}$$

In industrial, treatment electrochemical process is employed to reduce Cr(VI) to its Cr(III). This is achieved by the formation of ferrous ions from the anode into the solution upon the passage of direct current through the electrochemical cell. This process can be presented by the following reactions [31, 65]:

$$Fe(s) \longleftrightarrow Fe^{+2}_{(aq)} + 2e^{-}$$

$$6Fe^{+2}_{(aq)} + Cr_2O_7^{-2}{}_{(aq)} + 14H^{+}_{(aq)} \longleftrightarrow 6Fe^{+3}_{(aq)} + 2Cr^{+3}_{(aq)} + 7H_2O_{(l)}$$

During the electrochemical process, Cr(VI) reduction on the cathode could also occur

$$Cr_2O_7^{-2}{}_{(aq)} + 7H_2O_{(l)} + 6e^{-} \longleftrightarrow 2Cr^{+3}_{(aq)} + 14OH^{-}_{(aq)}$$

Reduction process is also employed by biological remediation as well phytoremediation which are environmentally friendly technologies [10, 13, 70, 71]. Bioremediation is the process of using biological products to help cleanup (remediate) areas that contain environmentally

hazardous products, such as: industrial, municipal waste and heavy metal contamination. The remediation can be implemented in several different ways depending upon the process that is being used and the targeted material for cleanup. Some examples are: introducing microbes into the contamination zone that digest and breakdown the chemicals into smaller and more environmentally friendly products, mineralization of the contamination by the microbes and cultivation of plants and/or trees that take up the contamination along with other nutrients and either breakdown these chemicals or store them within the plant tissues where it is more concentrated and easily harvested [10, 13, 72, 73]. Organic matter enhance the reduction of chromate in soil by increasing microbial activities, by acting as electron donors, and by lowering the oxygen (O_2) level of soil (oxygen is depleted through increased microbial respiration), thus creating reducing conditions. Some of the bacterial strains found to be resistant to high levels of Cr(VI) include *Pesudomonas fluorescens*, *P. aeruginosa*, *Enterobacter cloacae* and *P. mendocina* [74-77].

The phytoremediation is an emerging technology that uses various plants to degrade, extract, contain, or immobilize contaminants from soil and water [13, 28, 78-82]. This technology has been receiving attention lately as an innovative, cost effective alternative to the more established treatment methods used at hazardous waste sites. Some algae and macrophytes tend to concentrate metals to exceptionally high level and therefore help in reclamation of metallifferous effluent. Duckweed (*Lemnaceae*) has been considered as promising prospective scavengers of heavy metals from polluted waters [26, 83-85]. These rapidly growing plants exhibit relatively high tolerance to chromium toxicity and are capable of active uptake and accumulation of this element against its concentration gradient. Most of Cr(VI) is reduced to Cr(III) and retained by roots. Very little chromium is translocated to leaves. Trivalent chromium is believed to be precipitated and sequestered in the vacuoles of root cells.

I.2.2. Chemical precipitation

Chemical precipitation is the most common technology used to remove dissolved ionic metals from solution [14, 31]. The ionic metals are converted to an insoluble of particle by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and/or filtration. The effectiveness of a chemical precipitation process is dependent on several factors, including the type and concentration of ionic metals present in solution, the precipitant used, the reaction conditions (especially the pH of the solution), and the presence of other constituents that may inhibit the precipitation reaction [14].

Removal of Cr(VI) from wastewater by precipitation usually consists of two stages process, first, the reduction of Cr(VI) to Cr(III) and second followed by alkaline precipitation as chromium hydroxide. But the precipitation of heavy metals as hydroxide through the addition of lime is a well established technology which generates large volume of relatively low density sludge which could pose problems in sludge disposal [31, 66]. The standard reduction treatment technique is to adjust pH to three or below with sulfuric acid, and convert the Cr(VI) to Cr(III) using a chemical reducing agent such as sulfur dioxide, various sulfite compound or ferrous sulfate [66, 67].

First stage:

$$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ \longrightarrow 2Cr^{+3} + 6Fe^{+3} + 7H_2O$$

$$2Cr_2O_7^{-2} + 3S_2O_5^{-2} + 10H^+ \longrightarrow 4Cr^{+3} + 6SO_4^{-2} + 5H_2O$$

$$Cr_2O_7^{-2} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{+3} + 3SO_4^{-2} + H_2O$$

Second stage:

$$2Cr^{+3} + 3Ca(OH)_2 \longrightarrow 2Cr(OH)_{3(s)} + 3Ca^{+2}$$

I.2.3. Adsorption

Adsorption is the accumulation of atoms, molecules, or ions at the surface of a solid or liquid as the result of physical or chemical forces**.** Several sorbents have been employed to remove chromium from polluted waters, such as activated carbon [23, 55,-57], biopolymers [51, 86]), non-living microorganisms, mineral solids [66], soybean [15], bone charcoal that is a product obtained from the calcinations of bovine bones at high temperatures in the absence of air [60, 61], fly ash [59], sphagnum moss peat [87], *pinus pinaster* bark [88], leaf mould [89], coconut tree sawdust carbon [42], sawdust, cactus, olive stone/cake, wool [40, 90], charcoal and pine needles [60].

Activated carbon has been widely used in wastewater treatment to remove organic and inorganic pollutants. Possessing high surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds. The removal efficiency is influenced by the characteristics of the activated carbon, such as surface properties, area and chemical characteristics. In general, the characteristics of activated carbon are controlled by the manufacturing process. Depending on the nature of the raw materials, the nature of the activating agent and the conditions of the activation process, the properties of the activated carbon can be varied. The surface of activated carbon contains protonated C-OH_2^+, neutral C-OH or ionized C-O^- groups. It was found that chromium ions can be removed more effectively in an acidic environment with adsorption capacity increasing exponentially with decreasing pH. There are two types of activated carbons, H-type and L-type. H-type activated carbons assume positive charge (protonattion) upon introduction to water (yielding alkaline pH) and hence are hydrophobic, and can adsorb strong acids. Examples on H-type are coconut shell-based activated carbons, and dust coal activated carbons. H-type carbon can be lactones, quinones, phenols and carboxylates [41]. On the other hand, L-type activated carbons assume a negative charge (ionized) upon hydration (yielding acidic pH), and hence are hydrophilic, and can neutralize strong bases. L-type carbons are carboxyl, phenolic hydroxyl, carbonyl (quinone type), carboxylic acid, anhydrides, lactone and cyclic peroxide [41, 57, 58]. In the removal of Cr(VI) by carbonaceous material such as saw dust ; the groups (C_xO and C_xO_2) which are present on the surface of these materials, come into contact with water and hydrolyze it as shown below:

$$(C_xO \text{ and } C_xO_2) + H_2O \longleftrightarrow C_xOH_2^{2+} + OH^-$$

When the Cr(VI) ions are introduced into the system, they are adsorbed onto the positively charged surface [44] as follows:

$$C_xOH_2^{2+} + HCrO_4^- \longleftrightarrow C_xO_2H_3CrO_3^-$$

Biopolymers are a good sorbents for the heavy metals, such as proteins, cellulose, lignin, chitin, and chitosan. Chitin is second only to cellulose in terms of abundance in nature; also Chitosan can be produced chemically from chitin and is found naturally in some fungal cell walls. These polymers are inexpensive, abundant, and display high adsorbent efficiency for heavy metals due to the different functional groups that are present on their surface. For example, chitosan have a free amino acid and lignin have polyhydric phenol groups in addition to others [51, 91].

Biosorption of heavy metals by living and non-living microorganisms such as yeast, bacteria, fungi and algae has gained important credibility during recent years for the good sorption, low cost and availability of these materials [14, 17, 25, 44, 59, 73, 74]. These microorganisms are generated in large quantities as waste products from fermentation industries. The bisorption using dead biomass has major advantages over living one due to the lack of toxicity constraints, non requirement of nutrient supply and recovery of bound metal species by an appropriate desorption method [17, 20, 27, 50, 75].

Hexavalent Chromium is adsorbed by mineral solids that have exposed inorganic hydroxyl group on their surface including iron and aluminum oxides, kaolinite and montmorillonite. In the environment, iron oxides are the predominant adsorbents of chromium in acidic to neutral soils and ground water. Also Cr(VI) adsorbs more tightly to oxides and clay (silicate minerals) particles than other anions as chloride, nitrate, and sulfate [66, 92, 93].

Soybean is a very useful plant and was also employed in chromium removal [15]. Soya has abundant proteins and lipids and its bread is useful for diabetic patients because of high nutritional worth. Soybean cake has $–NH_2$ and –COOH and other functional groups. Each of these groups has reductive and adsorptive properties. The adsorptive property of these groups is due to the electrostatic forces between them and Cr(VI) or Cr(III) species [15]. The treatment efficiency of chromium using soya cake, increased as pH decreased and also as temperature increased [15].

Bone charcoal is an appropriate adsorbent for the Cr(VI) from aqueous solutions, the process being dependent on pH, contact time, mass of bone charcoal and chromium concentration as well as the volume of effluent treated. At pH 1 and a bone charcoal mass of two grams; Cr(VI) was found to be removed quantitatively in only 30 minutes from solutions having concentrations in the order of 10 ppm and in the presence of other ions or matrix components of real tannery effluents. The high efficiency of bone charcoal for the removal of Cr(VI) from complex mixtures opens also the possibility for using this material to clean analytical wastes [60, 61].

I.2.4. Ion exchange

Ion exchange is an important water treatment process that is particularly well suited to the removal of ions. The process employs specially charged materials, called ion exchange resins that can exchange one ion for another by holding it temporarily and releasing it to a regenerate solution. In ion exchange systems, polymeric resins are usually employed. Ion exchange using synthetic resins is the method of choice in many water treatment processes for removing inorganic contaminants in water and wastewater. The main advantages of

ion exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications [33-35]. It was found that more than 95% of chromium removal was achieved using two types of resins IRN77 and SKN1 that contain mainly sulfonic acid as functional groups [34].

I.3. Speciation methods

The term "speciation" in analytical chemistry refers to the separation and quantification of the different oxidation states or chemical forms of a particular element. Previously, the determination of total element concentrations was considered to be sufficient for clinical and environmental considerations [21, 94]. Although the total concentration of an element is still useful to know, and sometimes essential, the determination of species is necessary to fully understand the biogeochemical and toxicological behavior of metals. The speciation analysis of an element yields information on the individual concentrations of the various chemical forms of that element in environmental samples [94]. The extensive use of chromium compounds in various industries has resulted in the release of large quantities of chromium compounds to the environment. Cr(III) is essential to human health, and Cr(VI) is a poison and a carcinogen to humans. Therefore, total chromium measurement cannot be used to determine environmental impact due to the considerable difference in toxicity of the two elemental forms. For this reason, speciation of chromium has become very important [21, 94].

Speciation involves developing a high performance separation method, and detecting the separated components with high sensitivity. There are two main groups of chromium speciation methods, off-line and on-line [21, 94-99]. Off-line methods that are used in separation and preconcentration of a particular chromium species, and is carried out before the samples insertion into the detection instrument. The sample pretreatment techniques in the off-line methods include colored complex formation methods, soluble membrane filter technique [38, 39], chromatographic methods [98], electrochemical methods [31, 65], co-precipitation techniques, ion exchange techniques [32], separation using chelating resins and solvent extraction [37]. Spectroscopic methods are generally used for detection, including mainly UV-Vis spectrometry [100], atomic absorption spectrometry (AAS) [96], electrothermal atomic absorption spectrometry (ETAAS) [104] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [103].

On-line methods are the integration of separation system, with the detection system in consequence fashion. , Identification and quantification of chromium are carried out in a one step analytical process. Among the main separation-speciation techniques are: high performance liquid chromatography (HPLC) which includes ion chromatography (IC) [101, 105], ion-pair chromatography (IPC), [106] flow-injection analysis (FIA) [107] and reversed phase chromatography (RP) [100]. High performance liquid chromatography (HPLC) is a convenient technique for simultaneous determination of both Cr(III) and Cr(VI) species. Spectrometric methods are generally used for detection of the speciated chromium. Examples are: flame atomic absorption spectroscopy (FAAS) [96], direct current plasma atomic emission spectroscopy (DCP-AES), inductively coupled plasma atomic emission spectroscopy (ICP-AES) [103], and inductively coupled plasma atomic mass spectroscopy (ICP-MS) [98].

Chromatography involves a sample or sample extract being dissolved in a mobile phase, which may be a gas, a liquid or a supercritical fluid. The mobile phase is then forced

through an immobile, immiscible stationary phase. The phases are chosen such that components of the sample have differing solubilities in each phase. A component which is quite soluble in the stationary phase will take longer to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase. As a result of these differences in mobility, sample components will become separated from each other as they travel through the stationary phase. Techniques such as High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) use columns with narrow tubes packed with stationary phase, through which the mobile phase is forced. The sample is transported through the column by continuous addition of mobile phase. This process is called elution. The average rate at which an analyte moves through the column is determined by the time it spends in the mobile phase [108, 109].

High performance liquid chromatography (HPLC) is extensively applied to the determination and speciation of a number of metal ions [108, 109]. Methods combining HPLC separation with atomic spectrometry for highly sensitive selective detection of elements proved very promising. We also used this combination to speciate Cr(III) and Cr(VI) and developed the quickest automatic method in the literature by using a reversed phase C_{18} HPLC column and optimizing the parameters [110, 111].

Ion exchange chromatography involves the process of an analyte ion and ions of the mobile phase competing for oppositely charged functional group ions on the stationary phase. Both cation and anion exchange modes are used. Chromium species are separated on ion exchange columns. Among these, anion exchange columns are used on which only Cr(VI) species are retained directly, whereas Cr(III) passes without any retention. On the other hand, Cr(III) can be retained after its conversion into a negatively charged complex. Retention of two oxidation states of chromium was also achieved in the system with both anion and cation exchange columns connected in parallel or by using an anion exchange column containing a small proportion of cation exchange group to separate Cr(III) from Cr(VI). Cr(VI) was detected after its reduction. A cation exchange column was also applied for separation of Cr(VI) and Cr(III) complexes [105].

Capillary electrophoresis (CE) coupled to UV-Vis spectrometry is used as an alternative to the chromatographic methods [112 - 114]. CE method is based on the dual opposite end injection principle and contactless conductmetric detection. The sample containing cationic and anionic species is injected into the opposite ends of the separation capillary and after the high voltage is applied, the analytes migrate towards the capillary center, where the cell of a contactless conductivity detector is placed. The method does not require any sample pretreatment, except dilution with deionized water. CE generally offers better resolution and separation efficiency than chromatographic techniques. The major problem in their application for environmental samples is the small sample volume (several nanoliters) that requires a very sensitive detector to match the naturally occurring analyte levels. CE which offers certain advantages in this respect such as the ability to separate complex mixtures of ions very efficiently and rabidly, low operating costs, ease of operation and automation [115, 116, 117].

The flow-injection analysis (FIA) separation process is similar to batch filtration or solvent extraction procedures [107]. The separation columns are filled with: cellulose sorbents, chelating ion exchanger, complex forming resin, C18-bonded silica, polyether ether ketone and activated or modified alumina. By using a dual-column flow-injection manifold, the determination of both Cr(III) and Cr(VI) forms can be achieved. In a single-line flow-

injection manifold only one chromium form is determined directly, whereas the concentration of the other is calculated from the deference between the total chromium contents and that of the measured one. The advantages of flow-injection methodology in the chromium speciation study are its simplicity, rapidity and versatility [107].

I.4. Chromium toxicity

Chromium exists in different oxidation states in environmental water and soils. Dissolved chromium is usually found in natural waters in two different oxidation states, chromium(III) and chromium(VI). Due to the difference in toxicities of the hexavalent and the trivalent chromium, many attempts have been made to discriminate between the two species [2, 3, 5, 118]. Depending on its oxidation state, chromium can be either toxic or beneficial. Water soluble Cr(VI) in the form CrO_4^{-2} or $Cr_2O_7^{-2}$, is extremely irritating and toxic to human body tissue owing to its oxidizing potential and ease to permeate biological membranes [8]. Chromium in its trivalent form is an essential trace element for plants and animals; it is involved in glucose metabolism and nucleic acid synthesis. However, Cr(III) has also been shown to be a potential hazard, especially in the aquatic environment [7]. Mammalian in vitro tests have shown that trivalent chromium is a potential toxin, because it is a competitive inhibitor of many cellular processes. Due to its toxicity and mobility, Cr(VI) has often been considered more problematic than Cr(III) as a contaminant in the environment [7]. The main sources of chromium pollution are mining, leather tanning, the cement industry, dyes, electroplating, and production of steel, photographic material and corrosive paints [119, 6].

I.5. Detection of chromium

Many analytical methods are available for the detection of chromium at trace levels. Among these are flame atomic absorption spectroscopy (FAAS) [96], direct current plasma atomic emission spectroscopy (DCP-AES), inductively coupled plasma atomic emission spectroscopy (ICP-AES) [99, 104], and inductively coupled plasma atomic mass spectroscopy (ICP-MS) [98, 101, 111], UV-Vis spectrometry [100], atomic absorption spectrometry (AAS) [107], electro-thermal atomic absorption spectrometry (ETAAS) [117]. Total reflection X-ray fluorescence spectrometry (TXRF) and radionuclide X-ray fluorescence (XRF) used for solid samples detection. In this work Chromium was analyzed using instrumental methods such as AAS or ICP-AES, which are accurate and sensitive, but allow determination of only the total content of chromium in a sample [99]. The principle of ICP-AES and AAS are discussed below.

I.5.1. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

The principle of (ICP-AES) for determination of metals is as follows. An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency. A sample aerosol is generated in a nebulizer and spray chamber and then carried into the plasma through an injector tube. A sample is heated and excited in the high temperature plasma. The high temperature of the plasma causes the atoms to become excited. On returning to the ground state, the excited atoms produce ionic emission spectra. A monochromator is used to separate specific wavelengths corresponding to different elements, and a detector measures the intensity of radiation of each wavelength. A significant reduction in chemical interference is achieved. In the case of water with low pollution, simultaneous or sequential analysis is possible without special pretreatment to achieve low detection limits

for many elements. This coupled with the extended dynamic range from three digits to five digits, means that multi element determination of metals can be achieved [99, 103]. The chromium was detected at two wavelengths at 205.552 and 267.716 nm and the detection limits are 0.1 and 0.04ppm, using ICP-AES respectively. The wavelength 267.716 nm was chosen because it is the best.

I.5.2. Atomic absorption spectrometry (AAS)

It is used for determination of metals. It is based on the phenomenon that the atom in the ground state absorbs the light of wavelengths that are characteristic to each element when light is passed through the atoms in the vapor state. Because this absorption of light depends on the concentration of atoms in the vapor, the concentration of the target element in the water sample is determined from the measured absorbance. The Beer Lambert law describes the relationship between concentration and absorbance [96]. The flow rates of air and acetylene were 8 and 2 l min^{-1}.

I .6. Previous work

Removal of chromium was studied by others using different low cost adsorbents such as activated carbon [23], bone charcoal [60], soybean [15] and sphagnum moss peat [87]. In our laboratory, different low cost adsorbents as wool, olive cake, sawdust, pine needles, almond shells, cactus leaves and charcoal were utilized for removal of chromium ions from synthetic and industrial wastewater. The ability of these adsorbents to remove chromium by batch adsorption technique with stirring at 30 degree Celsius was investigated. The following selectivity order: wool> olive> sawdust> pine needle> almond shell> coal and finally cactus leaves was found for the sorption efficiency of chromium and this order was argued due to the concentration and type of functional groups found on the surface of these adsorbents.

The dependence of percentage removal of Cr(VI) on pH showed that maximum adsorption took place at pH 2. For all adsorbents; the percentage removal of Cr(VI) decreased below and above pH 2. It was found that, an increasing in the final pH of solution took place. This was explained by hydrolysis of the adsorbents in water. No removal of Cr(III) by any of the adsorbents was observed at pH 2 and the adsorption of Cr(III) reached maximum at pH 5.

Natural wool was found to be the best adsorbent of Cr(VI) while almond shell was the weakest adsorbent. The percentage removal of Cr(VI) by wool increased as the contact time increased from 0.5 to 2 hours until equilibrium established. The percentage removal was also increased as the wool concentration increased and it was found to vary from 37.2% at 2g (wool)/l to 81.3% at 16g (wool)/l. Also it was found that the percent removal decreased as the initial concentration of Cr(VI) increased. This decrease in adsorption may be attributed to the monolayer coverage of solute molecule on the surface of adsorbent. The Gibbs free energy $\Delta G°$ was calculated and it was found to be - 2.26 KJ /mol for wool and increased until 2.80 KJ/mol for Cactus; this means that the wool has the largest affinity for selective removal of Cr(VI) compared to the other adsorbents.

I.7. Study objectives

In this study, our aim is to use wool and sand as speciating adsorbents for chromium by utilizing the continuous flow technique. The continuous technique will be carried out by using columns packed with wool or sand. The effect of various parameters, such as pH, contact time, flow rate, initial metal concentration, adsorbent size, and wool dyeing with acid alizarin Violet N, (AVN) on the speciation and removal of chromium will be investigated and optimized.

II

EXPERIMENTAL

II .1. Instrumentation

Total chromium concentrations were determined by a VARIAN VISTA-charged Coupled Device Axial simultaneous Inductively Coupled Plasma-Atomic Emission Spectrometer (VISTA CCD ICP-AES) [103] with a concentric nebulizer and AA-2600 Atomic absorption Flame Emission Spectrophotometer (AAS), Shimadzo [94]. The (ICP-AES) was operated at the following operating conditions: forward power 1.2 Kw, Plasma flow 15 l/min. the pH of solution was measured with a MH-30G pH meter using combined glass electrode calibrated with buffers 4.00 and 7.00.

II .2. Materials

II .2.1. Preparation of adsorbents

The adsorbents used in this study are wool and sand. Wool was cut from sheep, washed with distilled water and detergent, dried then cut to 0.50, 1.0, and 2.0 cm length fiber prior to use. Sand was also washed with distilled water, dried then sieved to pass through a 18-mesh screen, then washing with 500 ml of 0.1% nitric acid.

II .2.2. Preparation of solutions

All chemicals used in the preparation were of analytical reagent (AR) grade $K_2Cr_2O_7$, NaOH and HCl. A 5000 ppm stock solution of Cr(VI) was prepared by dissolving 7.0719 g of AR grade $K_2Cr_2O_7$ in 500 ml of distilled water. A 5000 ppm Cr(III) stock solution was prepared by dissolving 12.8111 g of AR grade $CrCl_3.6H_2O$ in 500 ml of distilled water. Standard solution 0.05, 0.1, 0.5, 1, 2.5, 3.5, and 5 ppm Cr(VI) for determining chromium using ICP-AES were prepared by appropriate dilution of stock solution. Also standard solutions 1, 3, 5, 7, and 10 ppm Cr(VI) for determined chromium by ASS-6200. Analytical solutions were prepared by dilution of the stock solution with buffered solution pH 1. The buffer solution was prepared by dissolving 8.31 ml of 37% of HCl (density 1.186 g/1ml) in one liter distilled water and adjusted the pH by diluted solutions of 1M NaOH.

II .3. Adsorption experiments

The experiments were designed by using different columns made from glass which packed with wool, sand or different percentage mixing of both, figures [1, 2]. Some of these columns used in continuous elution which means that a particular volume of chromium was applied to the columns then eluted with blank buffer to study the leaching of chromium. Others columns used in continuous flow of the chromium solution which means that a particular volume of the different concentration of chromium solution were applied to the columns to study accumulation of chromium by the adsorbents that packed the columns. These experiments were carried out at room temperature to investigate the influence of pH, contact time, flow rate, initial concentration of chromium, adsorbents size, dyed wool with acid alizarin Violet N, (AVN) and different percentage mixing of wool and sand on the continuous adsorption technique.

- Most of chromium solutions were prepared in buffer solution pH 1.00 (0.1M HCl) and other in buffer pH 5.00. The pH of feed stock chromium (influent) was maintained constant at pH 1.00. Elution by blank buffer solutions of pH 1.00,

2.00,…8.00 was performed to study the effect of changing pH environment on the wool-chromium interaction.

- The flow rate was fixed by quick fit tap at the bottom of the columns. Two flow rate were used in this work 2.30 ml/min, and 6.0 ml/min.

- Different initial concentrations were used for the both species Cr(VI) and Cr(III).

- Adsorbent size and percent mixing; wool fiber length used in columns packing was 0.50, 1.0 and 2.0 cm and sand was 18-mesh size. Wool fiber length (0.50 cm) and sand (18-mesh size) mixed in different ratio (50.0% wool to 50.0% sand), (75.0% wool to 25.0% sand) and (90.0% wool to 10.0% sand) for some columns packing.

- Dyed wool with the acid dye AVN was utilized as stationary phase for some columns to compare with wool without dye. Wool (0.50cm size) was dyed with 0.20 and 0.40 g of acid alizarin Violet N (AVN). The dyeing wool happened by mordant dye. By adding 0.20 g and 0.40 g of dye to two different beakers contains 500 ml of 0.05M acetic acid. After heating the solution, 26.0 g of 0.50 cm wool was added to each beaker with stirring and gradually increased the temperature for one hour until solution boiling. After boiling for 15.0 minutes the solution cooled at room temperature. The dyed wool was then washed with distilled water several times until no bleeding happened for wool.

Continuous flow adsorption was carried out by using columns (internal diameter 24.0 mm, column length, 50.0 cm and length of wool in the column 19.0 cm and sand 19.0 cm). The compactness of the adsorbents for wool was different due to the wool fiber length (0.50, 1.0, 2.0 cm, the compactness was 0.29, 0.27, and 0.21 g/l respectively) and for sand was 1.4 g/l.

Columns were packed with a known mass of wool or sand is classified as, [figure 1 and 2]:

1. Columns that packed with wool or mixing both adsorbents in different percentage.
2. Columns that packed with wool.
3. Columns that packed with sand.
4. Three sequential columns that packed with wool or sand (three plates).

The columns were conditioned with distilled water and buffer solution pH 1.00 before feeding the chromium stock solutions. The reproducibility of the experiments was checked by using two trials for the same experiment at the same time.

Duckweed plants were collected from wastewater pond from Al-Aroub Agricultural Station and rinsed firstly with tap water and then with deionized water. The pond water was analyzed and found to have chromium. Several experiments were carried out in 1000 ml beakers using synthetic wastewaters contaminated with 7.0 ppm of Cr (VI). Two beakers used in the experiments one beaker (control beaker) contains 1000 ml of 7.0 ppm Cr(VI) and nutrition, the second one contains 1000 ml of 7.0 ppm Cr(VI), nutrition and 10.0 g of fresh duckweed. The temperature was controlled and maintained at 23, 25, 28 ºC

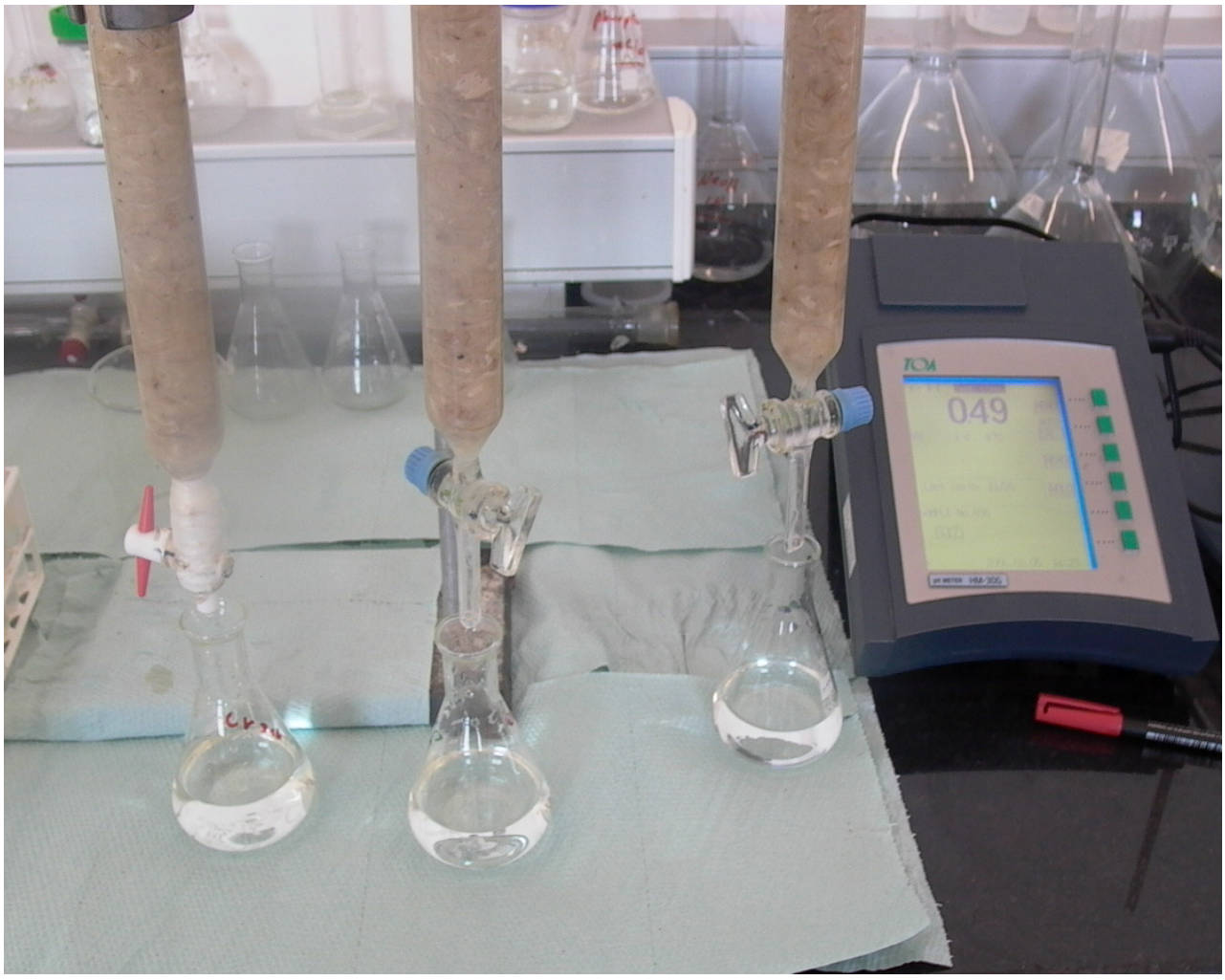

Figure [1], Columns of wool and sand

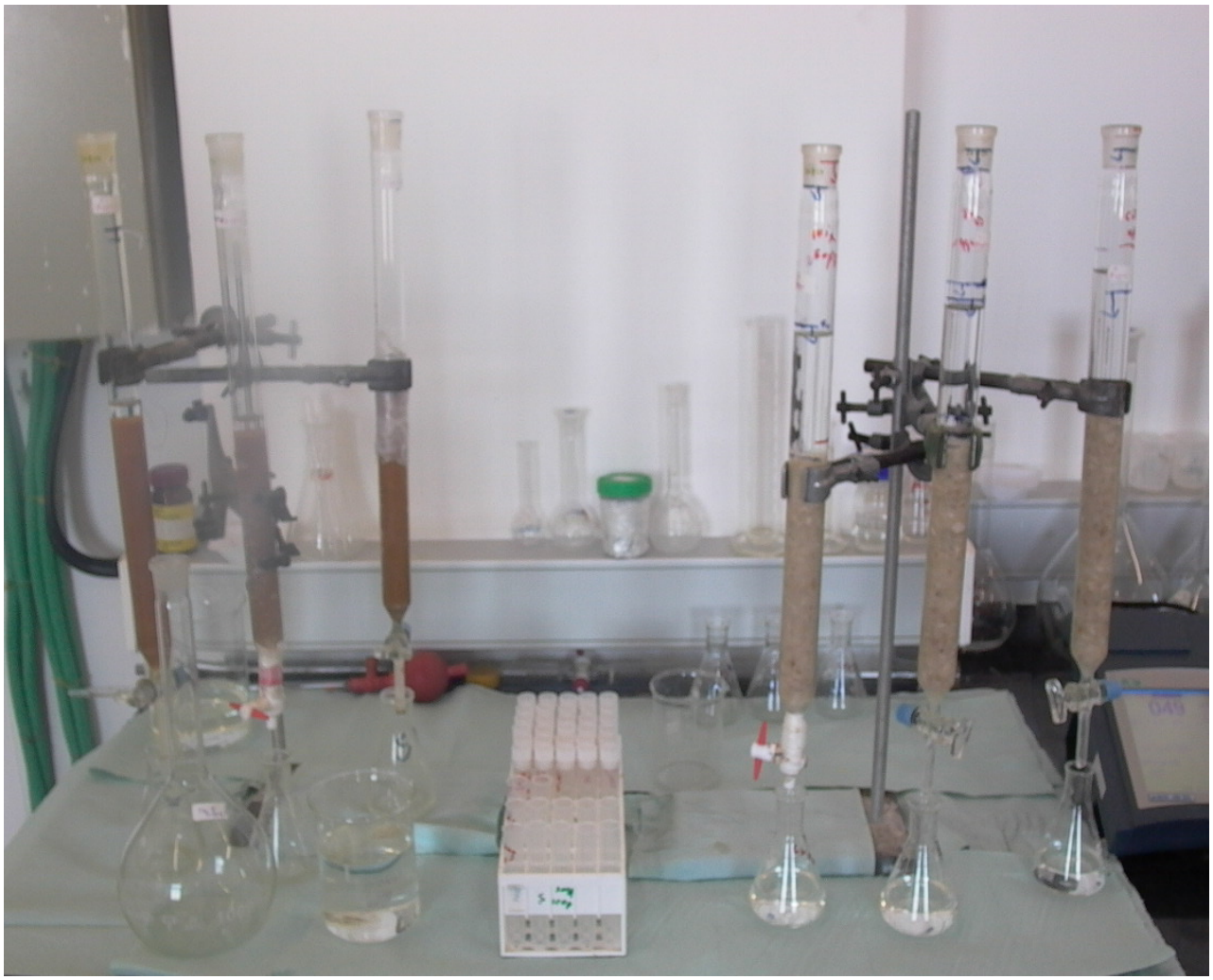

Figure [2], Columns of wool and sand

III

RESULTS AND DISCUSSION

III.1. Adsorption on wool/sand columns

The adsorption of Cr(III), Cr(VI) and a 1:1 mixture of both ions was tested at different columns packed with wool and sand. The metal ion solution was first applied to the columns at pH 1.00. The concentration of chromium in the leached was measured and consequently chromium uptake by the column was calculated. Buffer solutions of pH values 1-8 were then applied to the columns to test the stability of chromium adsorbed on the columns and if further leaching may take place. Data presented in table [1] shows that wool absorbed 48.7% of mixture of Cr(III) and Cr(VI) at pH 1, while sand absorbed 61.9%. Eluting the column by buffers of pH 1 to pH 8 did not result in significant leaching of either of the two forms of chromium. When the metal ion solution is applied to the columns at pH 5.00, wool absorbed 58.7% of Cr(III), 45.4% of Cr(VI) and 30.1% of mixture of Cr(III) and Cr(VI) after the columns were eluted with 1900 ml of buffer pH 5.00.

Utilizing different size (fibril length) of wool and mixing 0.50 cm of wool fiber with different ratios of sand for packing the columns has caused significant change on the flow rate of solutions but the fiber length of wool did not significantly affect the percentage removal of the 1:1 Cr(III)/Cr(VI) mixture until 2.0 cm length of wool fiber, table [2].

Table [1], Mass of Cr(III) , Cr(VI) and their 1:1 mixture were eluted from wool and sand columns loaded with 5.59 mg Cr(III) , 5.78 mg Cr(VI) and 5.89 mg of 1:1 mixture at room temperature and different pH. The elution volume was 500 ml, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth19.0 cm, sand size 18-mesh, sand weight 120.0 g and sand depth 19.0 cm.

Columns	Wool columns			Sand columns		
	Cr(III)	Cr(VI)	Cr(III)/Cr(VI) 1:1	Cr(III)	Cr(VI)	Cr(III)/Cr(VI) 1:1
Mass of Cr leached (mg) at pH1	5.59	0.835	3.02	0.385	3.94	2.24
Mass of Cr leached (mg) at pH2	0.00	0.899	0.368	0.00	0.00	0.00
Mass of Cr leached (mg) at pH3	0.00	0.0925	0.0434	0.00	0.00	0.00
Mass of Cr leached (mg) at pH4	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr leached (mg) at pH5	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr leached (mg) at pH6	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr leached (mg) at pH7	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr leached (mg) at pH8	0.00	0.00	0.00	0.00	0.00	0.00
Percent removal of Cr by absorbents (%)	0.00	68.4	41.7	93.1	31.8	61.9
Uptake s of Cr by adsorbents (mg)	0.00	3.95	2.46	5.20	1.84	3.65
Uptake of Cr (mg) / adsorbent (1 g)	0.00	0.152	0.0946	0.0433	0.0153	0.0304

Table [2], Mass of Cr(III) and Cr(VI) eluted from wool columns having different wool fiber length and columns packed with different percentage mixture of wool and sand by loading 2.91 mg of 1:1 mixture of Cr(III) and Cr(VI) at different pH and room temperature. The elution volume was 500 ml.

Columns packed with	50% 0.50cm size of wool	75% 0.5cm size of wool	90% 0.5cm size of wool	0.5cm size of wool	1cm size of wool	2cm size of wool
Mass of Cr mixture leached (mg) at pH1	1.10	1.23	1.18	0.946	1.05	0.883
Mass of Cr mixture leached (mg) at pH2	0.0303	0.0388	0.0606	0.136	0.125	0.109
Mass of Cr mixture leached (mg) at pH3	0.0205	0.0391	0.0673	0.0366	0.0571	0.0634
Mass of Cr mixture leached (mg) at pH4	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr mixture leached (mg) at pH5	0.00	0.00	0.00	0.00	0.00	0.00
Mass of Cr mixture leached (mg) at pH6	0.00	0.00	0.00	0.00	0.00	0.00
Percent removal of Cr mixture by adsorbents (%)	60.5	55.1	55.1	61.6	57.7	63.7

Comparing these results with previous data about adsorption of chromium by wool in batch experiment [(40)], it is important to recall that major differences should be taken into account to avoid misleading data interpretation. In batch absorption, the binding of chromium to the fiber was performed at each individual pH 1-5, some change between the initial pH (before adding Cr) and the final pH (after adding Cr) and finally, the swelling capacity of wool in the batch depended on the pH of medium not on the volume of solution [(40)]. However the adsorption process in this work is performed at pH 1.00, and then the reaction is perturbed by using different buffers of pH 1-8. No difference between pH initial and pH final due to the continuous flow of buffer and chromium solution and the swelling capacity of wool fiber was limited to the volume of the columns. These differences would affect the chemical and the structural forms of wool that consequently may result in variable mechanisms of interaction with the metal ion.

III.2. Removal of chromium(VI) by wool

The ability of wool fiber to sorb heavy metals ions like copper, cobalt, nickel, zinc and chromium from their aqueous solutions was early studied [10, 40, 90]. The good results achieved for the ability of wool to absorb metal ions from their effluent is argued to a direct consequence of the presence of many reactive sites in wool through which the metal can be linked. Wool is found to be a good adsorbent for hexavalent chromium at low pH by batch technique [40]. In this study, the continuous flow technique was used to remove chromium by wool. Using glass columns packed with wool fiber (stationary phase) and the columns have a quick fit tap to regulate the flow rate.

The continuous method gave a good result to remove Cr(VI) ions from their aqueous solution by using wool fiber as a stationary phase by passing Cr(III), Cr(VI) and 1:1 mixture of Cr(III) and Cr(VI) through wool columns. The solution of chromium prepared in buffer of pH 1.00 was allowed to flow through the columns then the columns were eluted five times sequentially using 100 ml of buffer solution of pH 1.00. The ion concentration was measured in the leached and the chromium retained on the fiber was calculated. Wool fiber showed a different behavior towards Cr(III) and Cr(VI). It is observed that wool adsorbed 85.6% (0.190 mg Cr (VI)/ 1 g wool), 48.7% (0.110 mg Cr mixture /1 g wool) and 0% of Cr(III) at pH 1.00. These results can be argued to the presence of Cr(VI) as $HCrO_4^-$ at low pH and its favorable interaction with the positively charged functional groups on the wool surface. The 0% removal of Cr(III) observed, is a result of the repulsion of the positive Cr(III) ions by the positively charged active centers on the highly protonated wool. These results are in full agreement with the previous work on batch adsorption [40]. The amount of the absorbed metal ion is calculated from the difference between the starting and residual ions in solution.

III.2.1. Effect of initial concentration of chromium(VI)

III.2.1.1. Continuous elution flow of Cr(VI)

Solutions of 4.55, 9.47, 47.9, 98.2, and 199 ppm of Cr(VI) were prepared and passed through glass columns packed with wool. 100 ml of each concentration were passed through the columns then the columns were eluted by 1000 ml of buffer pH 1.00. A grab sample after every 100 ml of buffer solution eluted is analyzed to measure chromium content. Constant flow rate, 2.30 ml/min, was achieved by adjusting the tap of the columns. The Cr(VI) in the leached was analyzed using the ICP and the uptake by wool was calculated, table [3]. Plot of uptake of mass of Cr(VI) (mg) per one gram of wool versus the initial concentration of Cr(VI), figure [3] shows a direct correlation. A little effect on the percent removal of Cr(VI) by the increasing the initial concentration of Cr(VI) is observed. This can be explained by the fact that as the concentration of Cr(VI) ions increases so does the metal loading capacity on the adsorbent, figure [4].

Table [3], Percent removal of Cr(VI) eluted from wool by loading of 0.455, 0.947, 4.79 9.82, and 19.9 mg of Cr(VI). The elution volume was 1000 ml at room temperature and pH 1.00. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

Concentration of Cr(VI) (ppm)	Percent removal of Cr(VI) by wool (%)	Uptake of Cr(VI) (mg) / 1 g wool
4.55	79.5	0.0141
9.47	82.5	0.0300
47.9	81.2	0.149
98.2	87.7	0.331
199	86.3	0.661

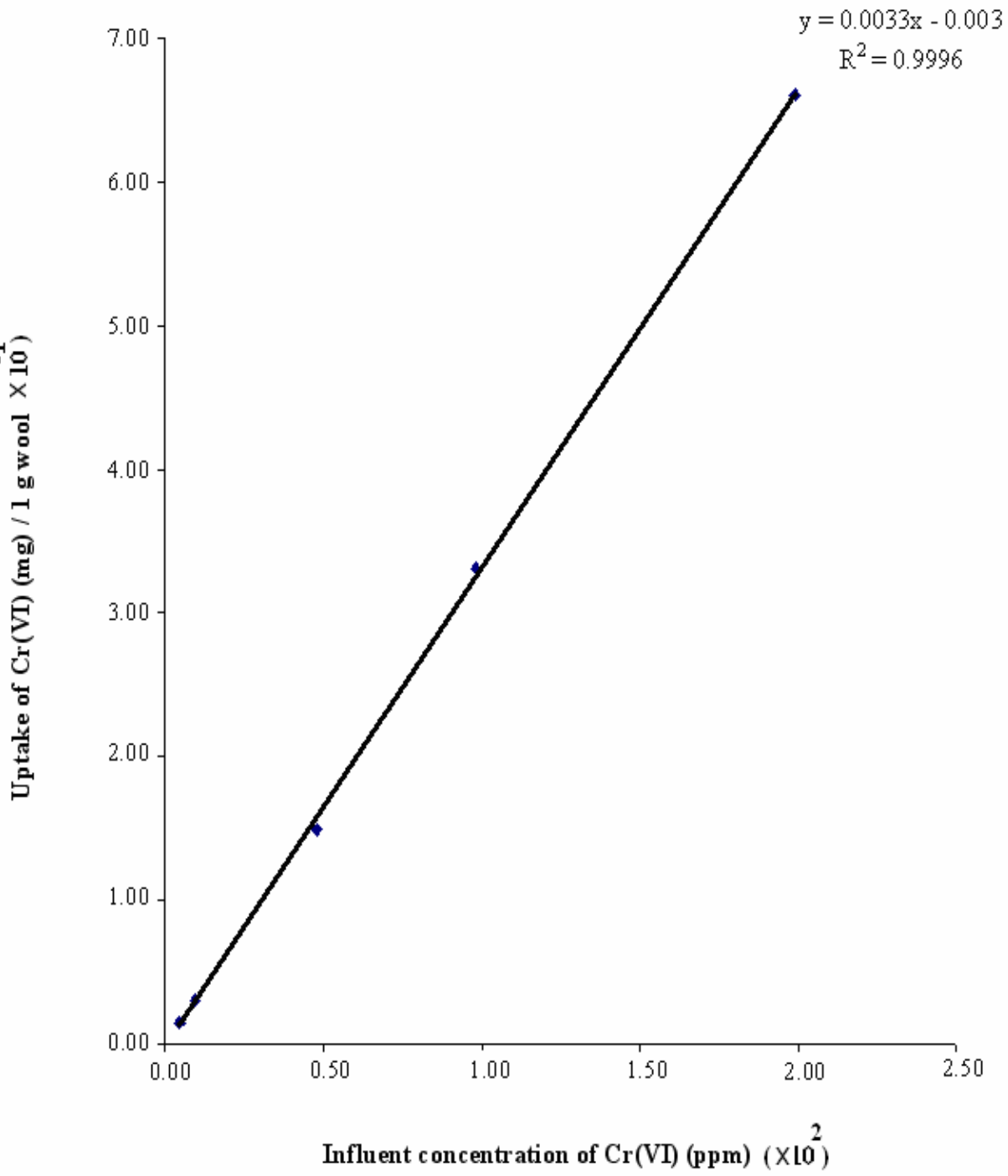

Figure [3], Mass of Cr(VI) uptake by wool after loading the wool columns with 0.455, 0.947, 4.79, 9.82, and 19.9 mg of Cr(VI). The elution volume was 1000 ml having pH 1.00 at room temperature. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm

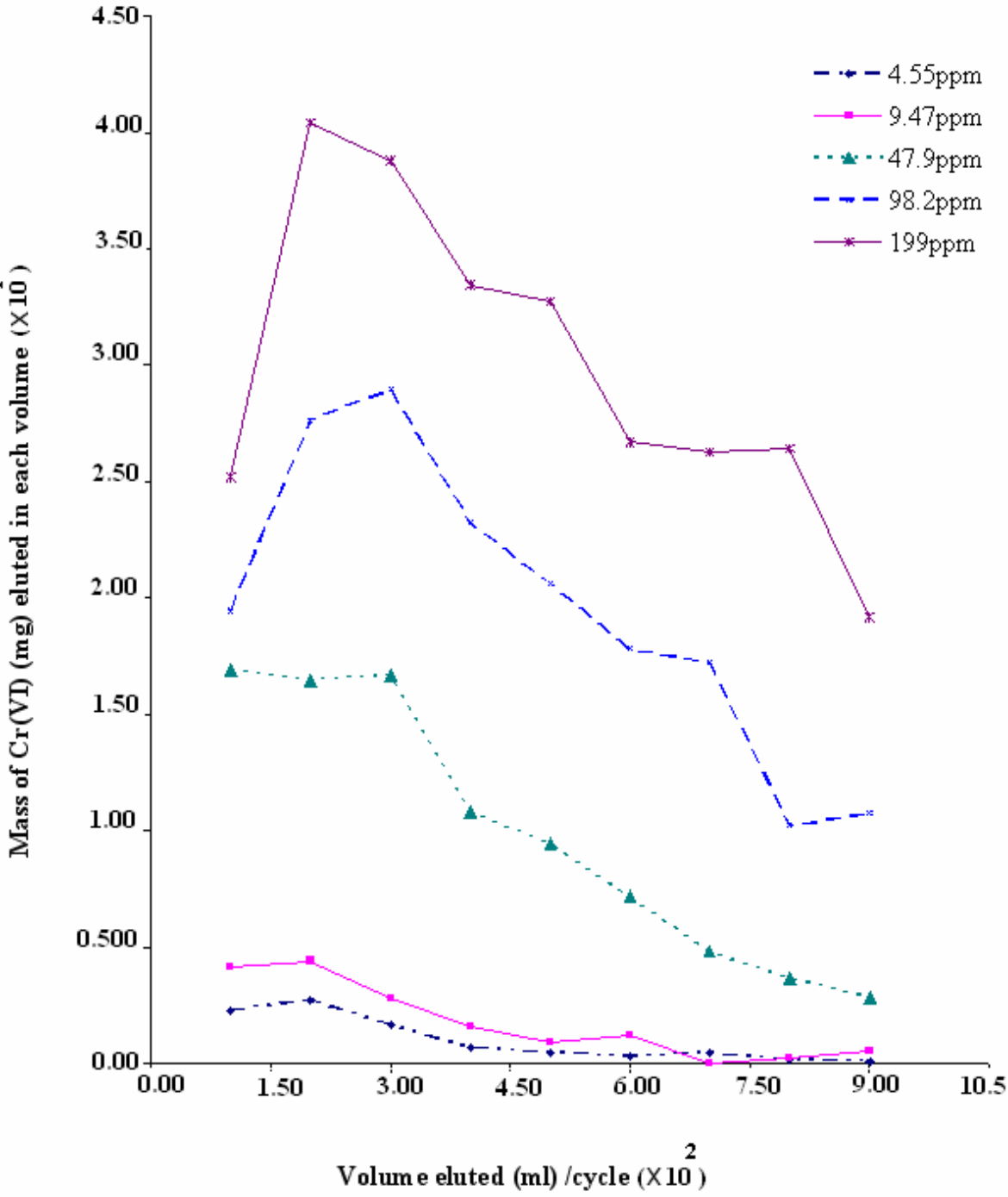

Figure [4] Mass of Cr(VI) eluted at different volumes of elution buffer from wool columns loaded with 0.455, 0.947, 4.79 9.82, and 19.9 mg of Cr(VI) at room temperature and pH 1.00. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm Each cycle 100 ml of buffer solution pH 1.00.

III. 2.1.2. Continuous flow of Cr(VI)

Figures [5A, 5B] show the effect of influent Cr(VI) initial concentration on the percentage removal of the metal ion by wool. Three liters of Cr(VI) solution of 5.09, 48.7, 100, and 208 ppm were prepared in buffer pH 1.00 and passed through the wool columns at constant flow rate, 6.0 ml/min. The amount of Cr(VI) absorbed by one gram of wool was 0.495 mg/g (84.3% removal) for the Cr(VI) initial concentration of 5.09 ppm. This was found to increase to 23.3 mg/g (97.0% removal) for the initial concentration 208 ppm at room temperature and pH 1, table [4]. It is clear from figures [5 A-B and 6] that a direct correlation between Cr(VI) initial concentration and the amount of mass of Cr(VI) (mg) removed by one gram of wool. The percentage removal also is increasing at higher initial concentration within the tested concentration range. This can be explained by the fact that as the concentration of Cr(VI) ions increases so does the metal loading on the adsorbent and high capacity of wool to adsorb more Cr(VI) ions. For example, a concentration of 208 ppm will have higher surface loading as compared to concentration of 5.09 ppm.

Table [4], Percent removal of Cr(VI) by wool for continuous flow by passing 3000 ml of different concentration of Cr(VI) through wool column at room temperature and pH 1.00. The flow rate was 6.0 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

Concentration of Cr(VI) (ppm)	Percent removal of Cr(VI) by wool (%)	Uptake of Cr(VI) (mg) / 1 g wool
5.09	84.3	0.495
48.7	91.4	5.14
100	94.8	10.9
208	97.0	23.3

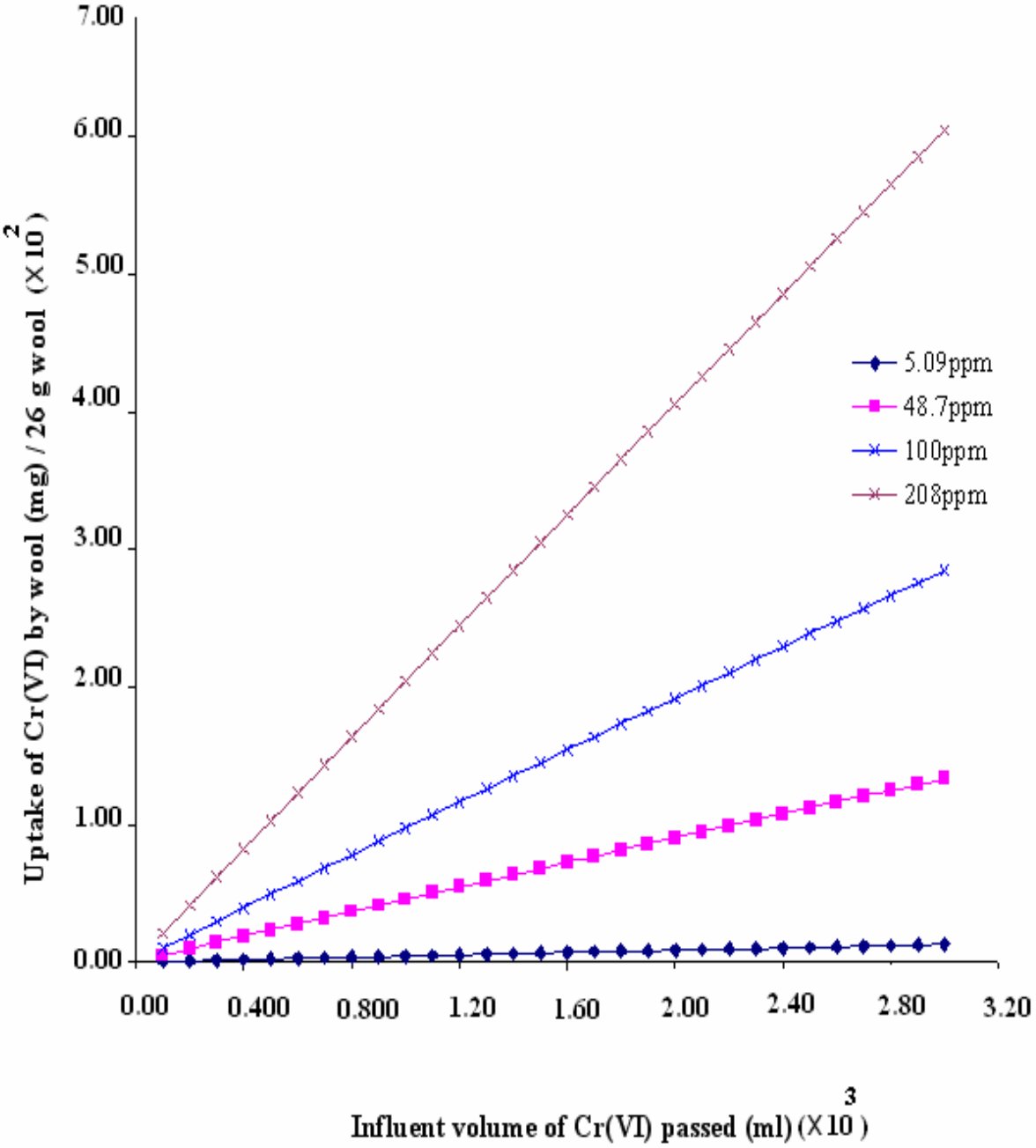

Figure [5A], Uptake of Cr(VI) by wool by passing 3000 ml of different concentration of Cr(VI) solution through wool column at room temperature and at pH 1.00. The flow rate was 6.0 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

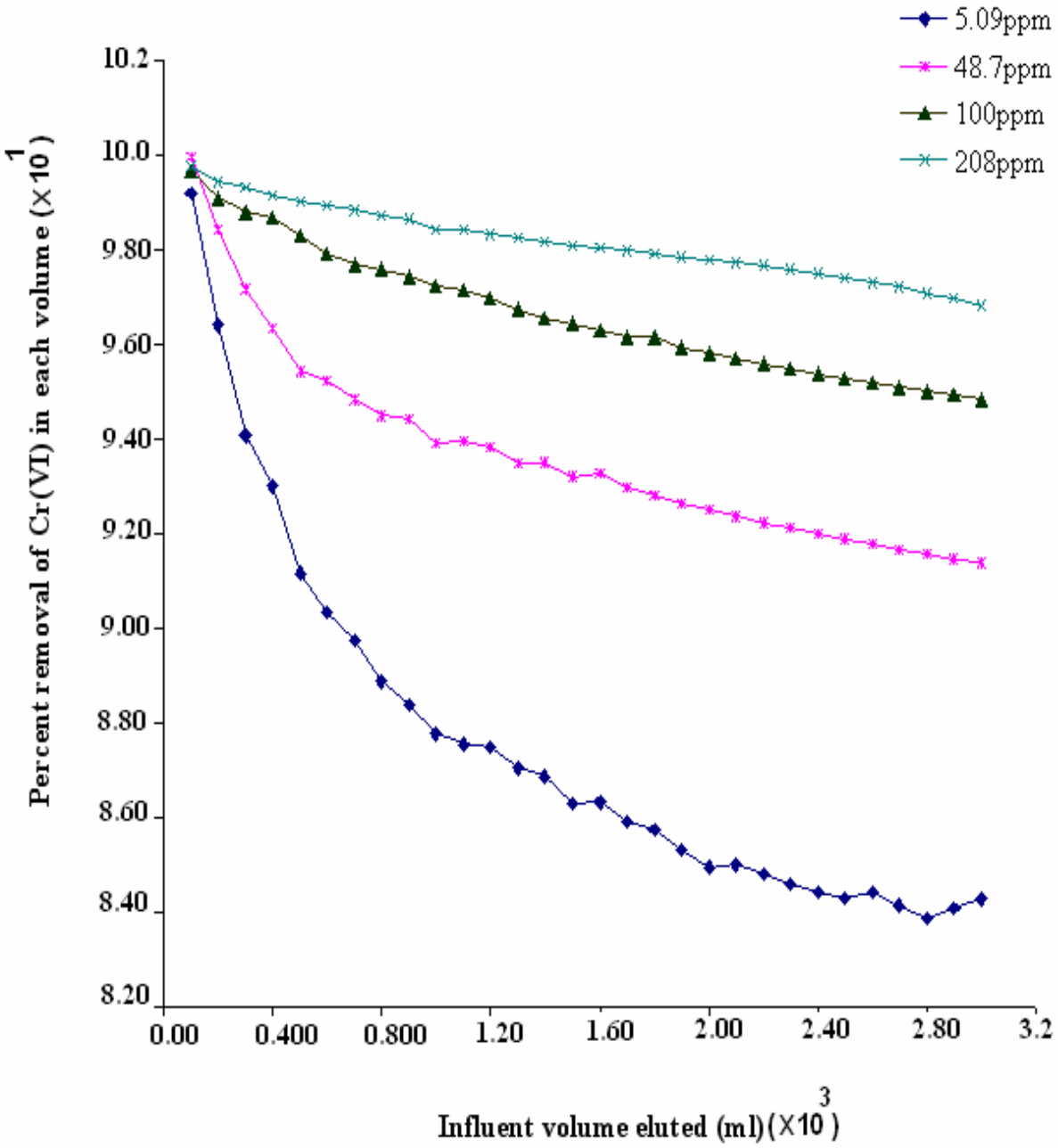

Figure [5B], Percent removal of Cr(VI) by wool by passing 3000 ml of different concentration of Cr(VI) solution through wool column at room temperature and pH 1.00. The flow rate was 6.0 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

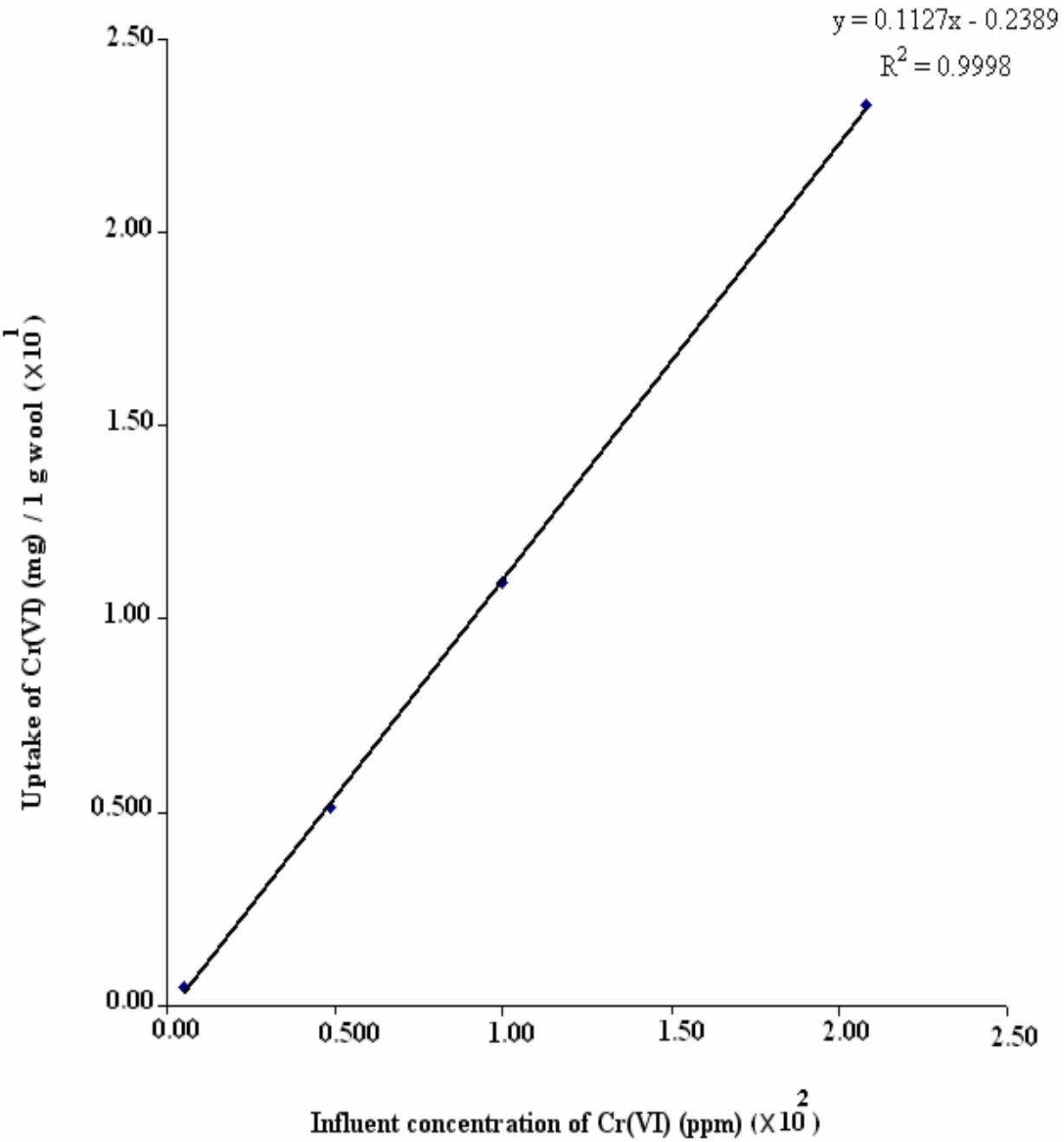

Figure [6], Mass of different concentration of Cr(VI) uptake by wool by passing 3000 ml of different concentration of Cr(VI) solution through wool column, at room temperature and pH 1.00. The flow rate was 6.0 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

III. 2. 2. Effect of dye on the percent removal of Cr(VI)

Usually, wool fiber is dyed from acidic medium using acid dyes. The interaction between the fiber and the dye molecule is known to be ionic and hydrogen bonding [40, 90]. In an attempt to study the competition between the dye and the Cr(VI) to bind to wool active sites, dyed wool with different concentrations of the Acid Alizarin Violet was utilized as substrate for columns. The effect of dye on wool's ability to sorb Cr(VI) ions from its aqueous solution was studied. The wool dyed with 0.20g/0.5l and 0.40g/0.5l of Acid Alizarin Violet N (AVN) is used in packing the columns and its performance is compared with and without dye. Three liters of 4.95 ppm Cr(VI) was passed through these columns at room temperature at flow rate 2.30 ml/min. Figure [7] shows a very small effect of the dye on the efficiency of chromium removal from its aqueous solution. The removal efficiency of Cr(VI) by wool without dye was 73.7% (0.421 mg Cr(VI) / 1 g wool), wool dyed with 0.20g/0.5l AVN was 74.8% (0.427 mg Cr(VI) / 1 g wool) and wool dyed with 0.40g/0.5l AVN was 74.2% (0.424 mg Cr(VI) / 1 g wool). This slight increase in chromium uptake may be argued to the possible formation of a ternary complex between the dye-metal-fiber. The rate of complex formation is relatively low compared to wool mordanting due to the low pH.

Despite the fact that the dyed wool was washed several times by distilled water and buffer pH 1.00 and during the conditioned of columns the solution was clear. However when Cr(VI) was added to the columns some bleeding of the dye and the color of solution eluted for 0.40 g AVN was darker than the color of 0.20 g AVN. This could be explained as a result of Cr(VI) competing with the dye on the active groups on wool surface. Consequently, some Cr(VI) ions displaced the dye molecules. Further future work is needed in this regard to investigate the effect of pH, changing dye and using different concentration of Cr(VI).

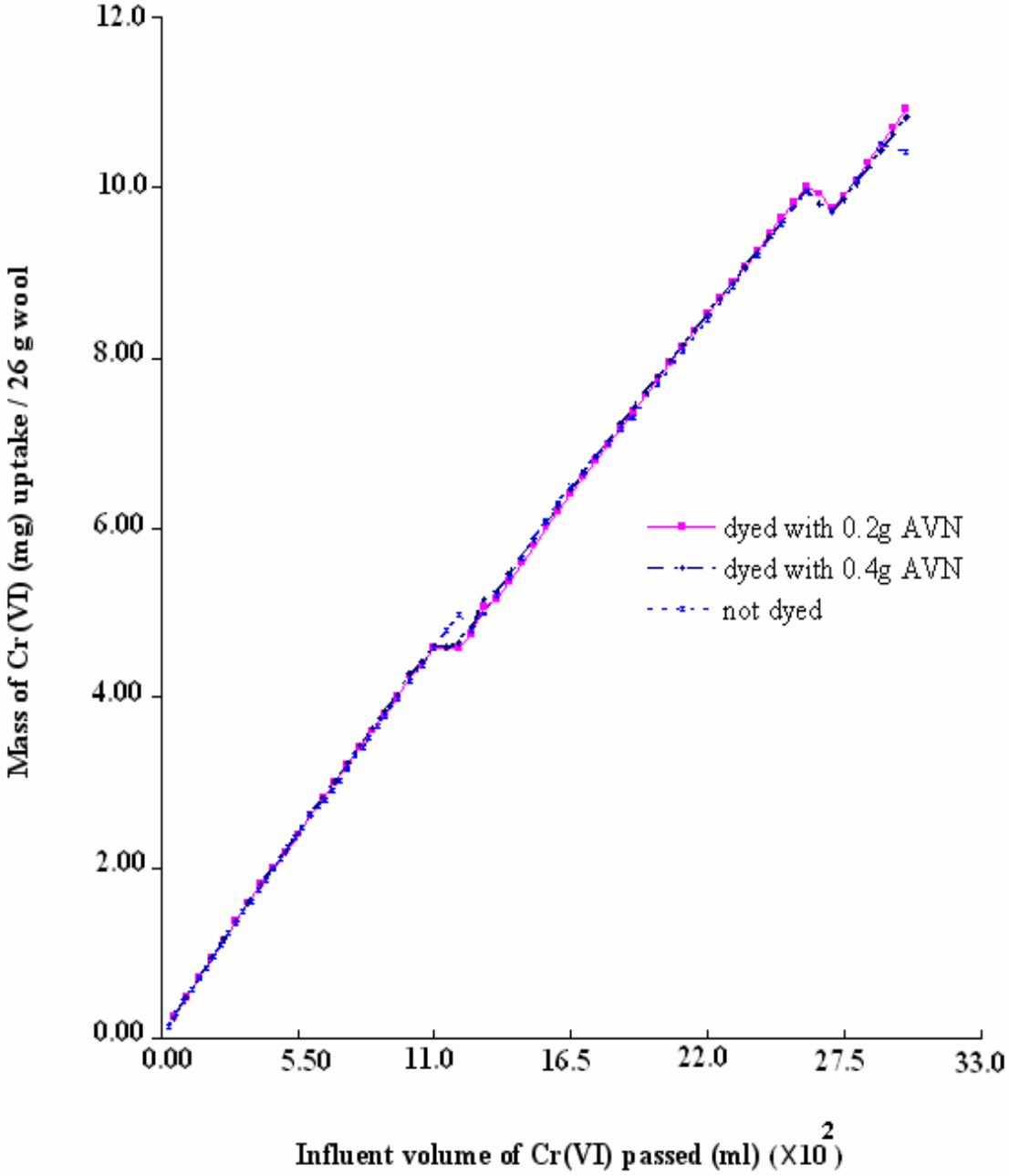

Figure [7], Mass of Cr(VI) uptake by wool, wool dyed with 0.20 g of AVN and wool dyed with 0.40 g of AVN by passing 3000 ml of 4.95 ppm Cr(VI) solution through wool column, at room temperature and pH 1.00. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

III. 2.3. Effect of flow rate

The effect of Cr(VI) solution flow rate inside the column on the percentage removal of the metal ion by wool was investigated. At first, the adsorption was carried out at flow rate 2.30 ml/min and then changed to 6.0 ml/min. One liter of 5.09 ppm of Cr(VI) solution was passed through the wool column at two different flow rates. The results showed that no effect of the flow rate on the percentage removal of Cr(VI) by wool from aqueous solution. It was found that 87.0% removal of Cr(VI) for both flow rate 2.30 and 6.0 ml/min, table [5]

Table [5], Percent removal of Cr(VI) by wool column loaded with 5.09 mg of chromium at different flow rates. Elution was performed with 10 aliquot of 100 ml at room temperature and pH 1.00. Wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

Volume of Cr(VI) (ml) eluted	Mass of Cr(VI) (mg) **X 10^{-2}** eluted at flow rate 2.30 ml/ min	Mass of Cr(VI) (mg) **X 10^{-2}** eluted at flow rate 6.0 ml/ min
100	0.707	0.422
200	3.64	3.23
300	4.54	5.41
400	5.50	5.18
500	10.8	8.28
600	6.40	7.00
700	8.50	7.03
800	7.78	8.80
900	8.28	7.90
1000	10.2	9.05
Percent removal of Cr(VI) by wool	87.0	87.8

III.2.4. Effect of contact time

The effect of contact time on the adsorption of 5.01 ppm Cr(VI) using wool columns at room temperature and pH 1.00 was also studied and the data is presented in table [6]. Before starting elution the solution of Cr(VI) was left in contact with the first column for 43.0 minutes and for 300 minutes in the second column. It is obvious that the increase in contact time from 43.0 to 300 minutes did not affect the percent removal of Cr(VI), which was 80.0%, figure [8]. The sites on wool can be dived kinetically distinguish two sites, one that is easy to remove and other take long time to remove. For contact time 43.0 minutes, there is no time for Cr(VI) to be on weak site but in strong one and therefore it took more time for chromium leached. But for contact time 300 minutes, there is enough time for chromium to be on weak and strong sites and so it took less time for chromium leached, figure [8]. The relation between contact time of the chromium solution and the retention of the mobile phase (buffer solution) in contact with wool fiber is another reason that may explain the faster leaching in case of longer contact time. Wool usually undergoes partial hydrolysis and structural arrangement in solution. When the column is stationary, wool undergoes hydrolysis and OH^- is released from this process and cause local pH change at the wool chromium binding sites. This leads to weaken the wool-chromium interaction at some sites and causes faster leaching.

Table [6] Percent removal of Cr(VI) by wool loaded with 0.501 mg of Cr(VI) as function of contact time. Elution was performed with 10 aliquots of 100 ml at room temperature and pH 1.00. Wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

Contact time (minutes)	43.0	300
Percent removal of Cr(VI) (%)	80.0	79.5
Uptake of Cr(VI) (mg) by wool	0.401	0.398
Uptake of Cr(VI) (mg) / 1 g wool	0.0154	0.0153

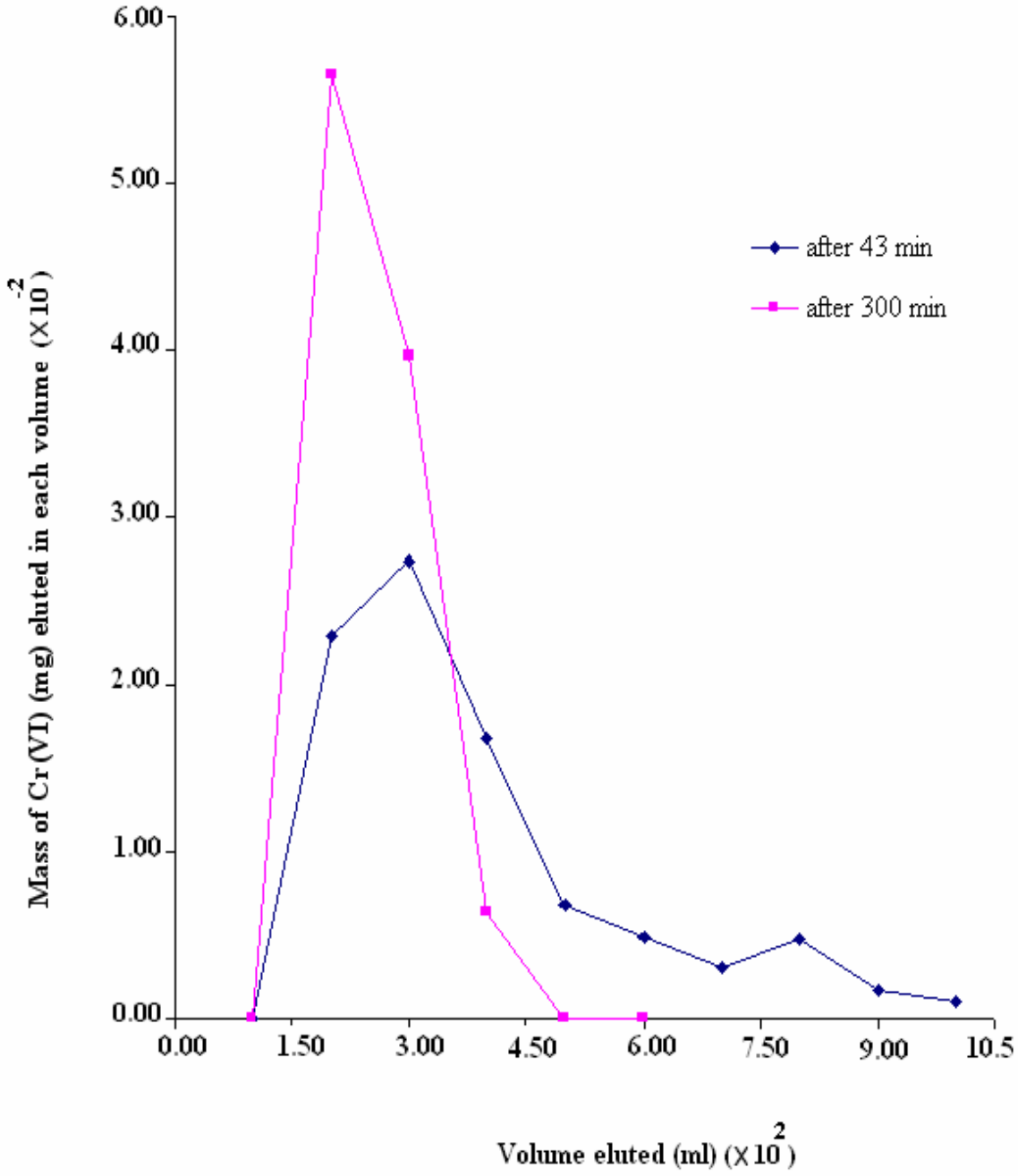

Figure [8], Mass of Cr(VI) leached from wool loaded with 0.501 mg of Cr(VI) as function of contact time. Elution was performed with 10 aliquots of 100 ml at room temperature and pH 1.00. Wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

III. 2.5. Effect of pH

In solution, hexavalent chromium exists as bichromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ionic species [40]. The stability of these forms is mainly dependent on the pH of the system. The $HCrO_4^-$ is the predominant species of Cr at pH 1-4. When pH increases, a shift of the $HCrO_4^-$ concentration to the other forms, CrO_4^{-2} and $Cr_2O_7^{-2}$ [40], takes place. Hence at pH 1, the $HCrO_4^-$ is the form adsorbed on wool [40].

The Cr(VI) adsorbed at the wool column at pH 1.00, 85.64% of the inlet concentration, was stable at the column when the column was eluted by different buffer solution pH 1, 2, 3, 4, 5 and 6. The wool columns showed that no differences in pH of the influent and effluent through the wool columns. This is due to the continuous flow of the excess buffer through the column which prevented local change in the pH inside the column. Most chromium removal from the column by continuous elution took place at pH 1, some at pH 2 and 3, and no chromium was found at the leached at pH 4, 5 and 6, tables 1 and 2.

III. 2. 6. Effect of addition Cr(VI) with continuous elution.

Several cycles of 100 ml of 4.87 ppm Cr(VI) solution were passed through the wool column. After each cycle and before passing the next one, the column was eluted by one liter of buffer pH 1.00, the Cr(VI) in the leached was measured, and Cr(VI) adsorbed on the column after each cycle was calculated. The results displayed in table [7] and represented in figure [9] shows a direct correlation between the applied mass of Cr(VI) to the wool column and the mass of Cr(VI) adsorbed per one gram of wool.

Table [7], Removal of Cr(VI) by wool loaded with seven times (cycles) 0.487 mg of Cr(VI). After each cycle the elution volume was 1000 ml of buffer solution at room temperature and pH 1.00. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

Mass of Cr(VI) applied to column	Uptake of Cr(VI) (mg) by wool	Uptake of Cr(VI) (mg) / 1 g wool	Percent removal of Cr(VI) by wool (%)
0.487	0.361	0.0139	74.2
0.974	0.753	0.0289	77.3
1.46	1.08	0.0415	74.2
1.95	1.44	0.0554	73.8
2.44	1.85	0.0712	75.9
2.92	2.19	0.0842	75.2
3.41	2.40	0.0923	70.5

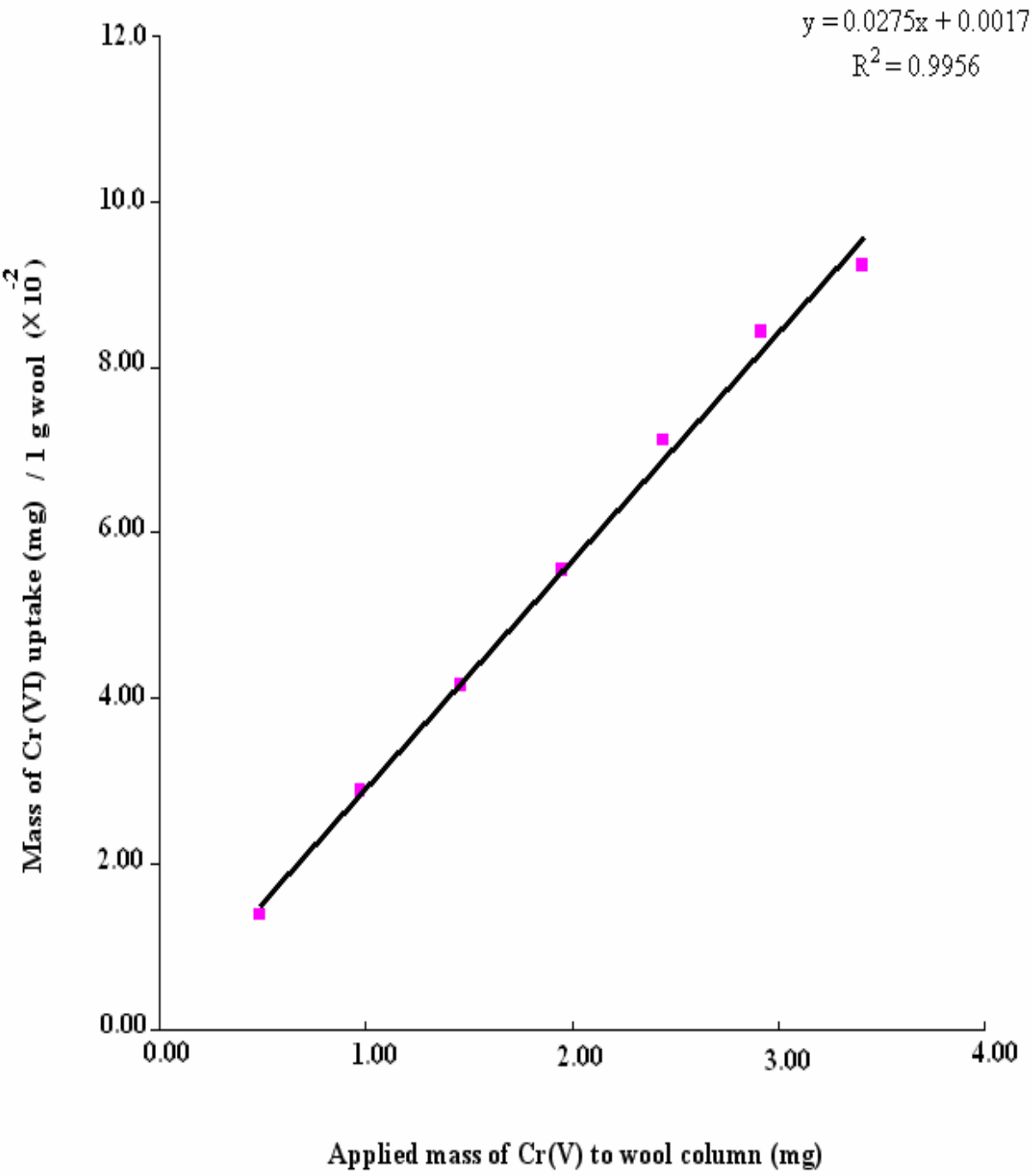

Figure [9], Mass of Cr(VI) uptake by wool loaded with seven times (cycles) 0.487 mg of Cr(VI). After each cycle the elution volume was 1000 ml of buffer solution at room temperature and pH 1.00. The flow rate was 2.30 ml/min, Wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.

III .2.7. Effect of column depth

The effect of column depth on the adsorption of 48.6 ppm Cr(VI) using Three sequential columns (three plates and the length of three plates was 57.0 cm) and one column (one plate and the length of plate was 19.0 cm) packed with wool at room temperature and pH 1.00 was also studied and the data is presented in table [8]. 100 ml of 48.6 ppm Cr(VI) was passed through the columns then the columns were eluted by 1000 ml of buffer pH 1.00. A grab sample after every 100 ml of buffer solution eluted was analyzed to measure chromium content. Constant flow rate, 2.30 ml/min, was achieved by adjusting the tap of the columns. The percentage removal of chromium for each was the same about 81.0% but the mass of Cr(VI) (mg) uptake by one gram of wool was 0.05 for three plates and 0.15 for one plate which is the three times bigger of three plates.

Table [8], Effect of column bed depth on the percentage removal of Cr(VI) by wool loaded with 4.86 mg of Cr(VI). The elution volume was 1000 at room temperature and pH 1.00. The flow rate was 2.30 ml/min, and wool fiber length 0.50 cm.

Depth of column	57.0 cm (78.0g weight of wool)	19.0 cm (26.0 g weight of wool)
Percent removal of Cr(VI) by wool (%)	84.3	81.2
Uptake of Cr(VI) (mg) by wool	4.09	3.95

III. 2.8. Desorption thermodynamics

It was observed from analysis of the first grab sample after the column is left overnight that the concentration of Cr(VI) in leached solution abruptly increased. The increase of Cr(VI) concentration was dependent on the time that the column was left and initial concentration of Cr(VI) passing through the column, figure [10]. The presence of many reactive binding sites on the wool fibril renders the mechanism of metal binding to the fiber complex. Some of the metal binding to the fiber is irreversible physi-sorption and others may be of reversible binding nature. When the contact time between the Cr(VI) solution and the column increases, in other meaning when the column is left overnight the flow rate is then 0.0 ml/min. This means the column behaves as a batch reactor in which local change at pH took place due to the release of OH^- ions from the wool fiber. This increase of pH would release Cr(VI) from the reversible binding sites of wool and consequently increase its concentration in the leached once the column is reactivated. After the solution inside the column starts to flow, the pH inside the column refreshes and the performance of the column again retained as steady as before it was left overnight.

The desorption of Cr(VI) from wool was dependent on the time and temperature. For a column packed with wool size 0.50 cm and initial mass of Cr(VI) on the column was 604 mg, increasing time and temperature increased desorption. When the temperature was increased from 20 to 35°C at pH 1, the desorption of Cr(VI) was found to increase from 7.11 mg/g (30.6% leached) to 8.80 mg/g (37.9% leached), figure [11]. The process of Cr(VI) desorption can be summarized by the following reversible process.

The equilibrium constant K_c is given by [120],

$$K_c = ((M_i - M_L) / M_i) * M_L \text{ ……..(1)}$$

Where,

M_i Initial mass of Cr(VI) on wool
M_L Mass of Cr(VI) leached

Substitution of equilibrium constant into equation (1) will yield K_c at different temperatures (see table 9).
The enthalpy of desorption (ΔH°) is obtained using the integrated Van't Hoff equation:

$$\ln K_c = (- \Delta H° / RT) + C \text{……(2)}$$

Where,

ΔH° Enthalpy change
T Temperature in Kelvin
R Gas constant = 8.314 J/ K mol
C Constant

A plot of $\ln K_c$ vs. 1/T will yield a straight line with a slope = - ΔH° / R, figure [11]. The value of ΔH° was found to be 5.30 kJ /mol.

The Gibbs energy of desorption can be calculated from

$$\Delta G^\circ = -RT (\ln K_c) \text{ ..……...…...(3)}$$

Where,

ΔG° = Free energy

The entropy of desorption ΔS° is obtained from

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{…….……(4)}$$

Hence,

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/ T$$

And values are found in table [9].

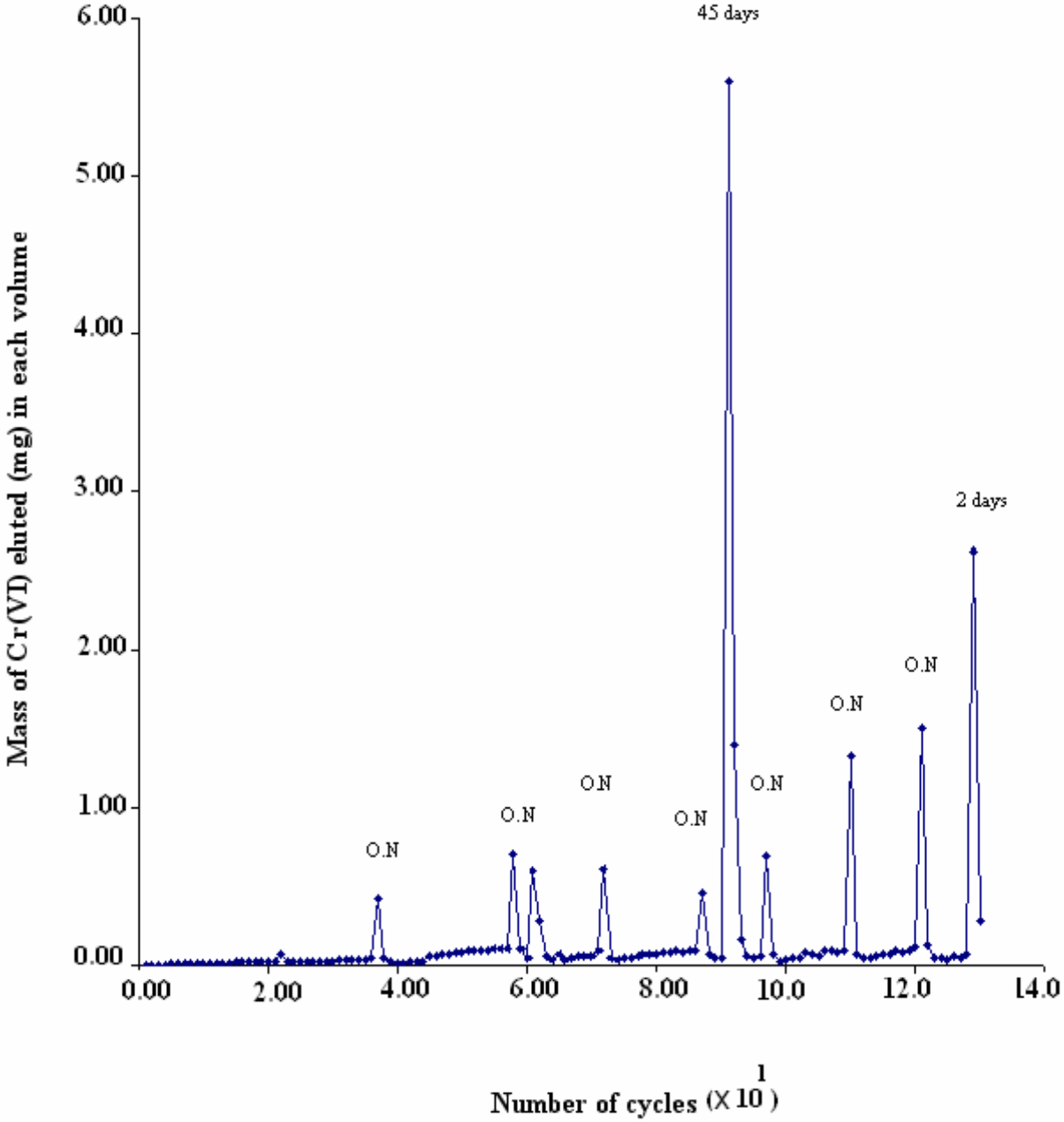

Figure [10], Mass of Cr(VI) eluted in each volume by passing $10.0*10^3$ ml of 5.09 ppm Cr(VI) solution through wool column, at room temperature and pH 1.00. The flow rate was 2.30 ml/min, wool fiber length 0.50 cm, wool weight 26.0 g and wool depth 19.0 cm.
O.N. over night
Each cycle 100 ml of buffer solution pH 1.00

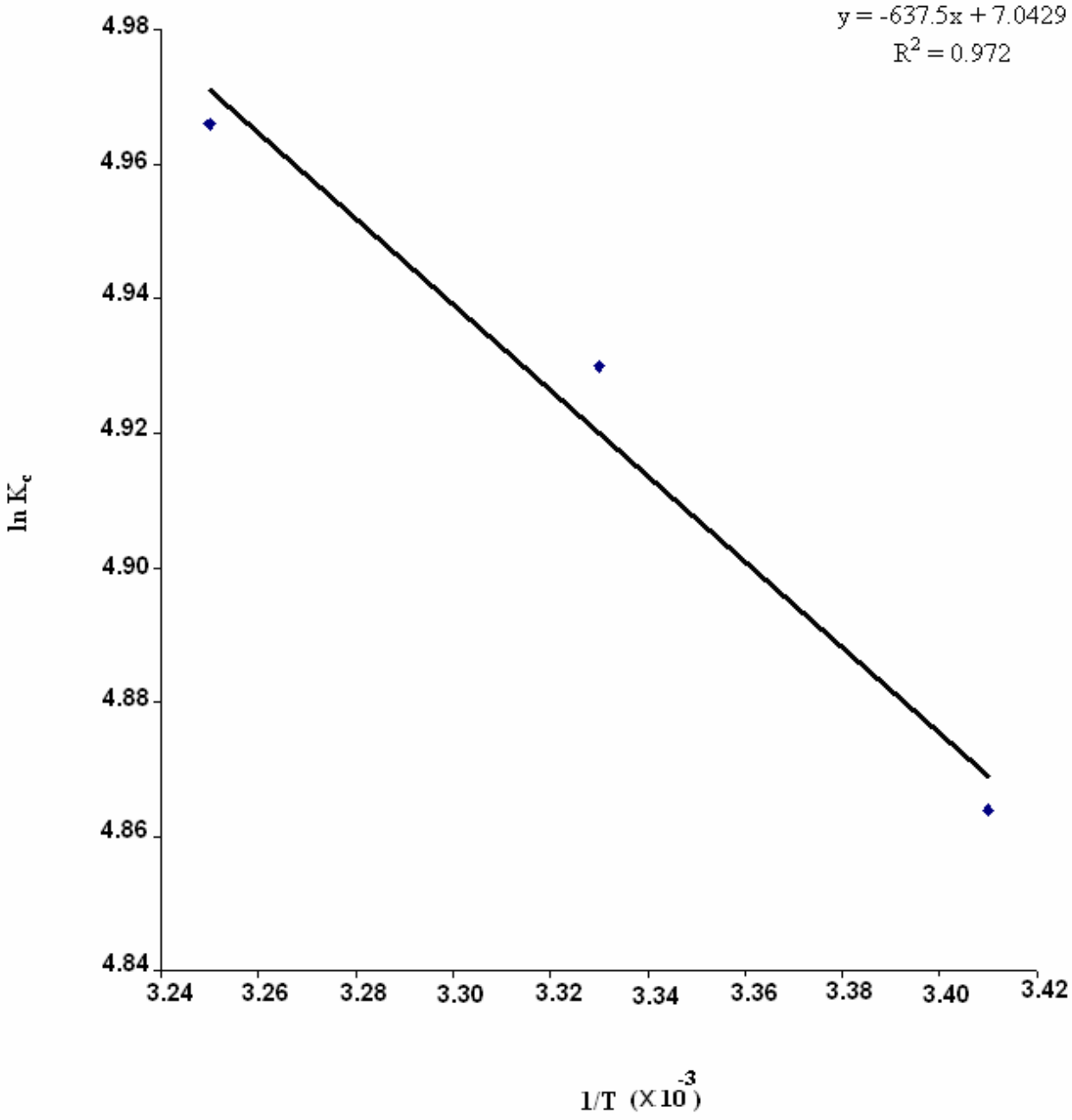

Figure [11], Van't Hoff plot for the desorption of Cr(VI) from wool by adding 3000 ml of buffer pH 1.00 on wool contain 604 mg of Cr(VI) with stirring for 180 minutes and took 5 ml for 15.0 times from solution for analysis during 180 minutes at different temperature (20, 27, 35 °C), and wool fiber length 0.50 cm, wool weight 26.0 g.

Table [9] Thermodynamic parameters for the desorption of Cr(VI) from wool at different temperature (20, 27, 35 °C), and wool fiber length 0.50 cm , wool weight 26.0 g .

Temperature / ºC	K_c	Δ G°/ (KJ /mol)	ΔS° / (J /mol K)
20	129.5	-11.85	58.53
27	138.4	- 12.29	58.66
35	143.5	- 12.72	58.50

The positive value of enthalpy change ΔH° indicates that the desorption process is endothermic. The negative values of free energy ΔG° at different temperature indicate the spontaneous nature of desorption. The positive value of entropy ΔS° showed increased randomness at the solid / solution interface during the desorption of Cr(VI) from wool.

Since, the desorption was endothermic, hence the amount adsorbed at equilibrium must increase with increasing temperature, because ΔG° decreases with the rise in temperature of the solution. This explains why the value of ΔG° becomes more and more negative with the rise in temperature of desorption.

III.3. Removal of chromium(III) by sand

In previous studies, good results were obtained on the ability of sand to sorb heavy metals ion like zinc (Zn), chromium (Cr), cadmium (Cd), copper (Cu), and Lead (Pb) from their aqueous solutions [121 -123]. Sand showed a good adsorbent for zinc at pH 3 and 7, and the removal efficiency from 71 to 87% with a maximum adsorption occurred at the column depth one meter as compared to 0.6 and 0.8 meter. The pH of solution did not have a significant effect on the removal efficiency of zinc by sand and at high pH the zinc precipitated as instead of permanent adsorption [122]. Sand used for removal of Cr(III) at pH 4 and 10 and showed high removal efficiency 92% and 98% for the concentration of 250 ppm respectively [121]. The results showed that the pH did not have a major effect on the removal of Cr(III) and the differences in removal was explained by the precipitation of chromium hydroxide at high pH [121]. The removal efficiency decrease with increasing concentration of chromium and also decreasing with increasing injection rate of the influent solution. The removal efficiency is increasing with increasing depth of sand column. Also the turbidity of solution was studied and it was observed that the turbidity removal efficiency increases with increasing depth of sand column and decreases with increasing injection rate [121].

III.3.1. Effect of initial concentration of Cr(III)

Figures [12 A-C], shows the effect of influent concentration on the removal of four different Cr(VI) concentrations: 4.95, 49.1, 98.3, and 206 ppm by passing three liters of these solutions, prepared in buffer pH 1.00, on sand filter. It is evident from figures that with a lower concentration of adsorbate the amount of Cr(III) attained on the sand are smaller than the amount attained when higher initial concentrations are used. However the percent removal of Cr(III) was greater with lower concentration and smaller with higher initial concentration.

The percentage removal of chromium by sand reached 93.1% for 4.95 ppm Cr(III) and 90.2% for 206 ppm Cr(III), also the breakthrough point curves affected by the initial concentration of chromium and it is shown in figure [12A]. It can be seen that a rise in the influent metal concentration reduces the volume treated before the packed bed gets saturated. A high metal concentration may saturate the sand more quickly, thereby decreasing the breakthrough time. Similar results were also obtained for the sorption of lead into sawdust [124] and these results agreed with the bed depth service time model (BDST) [124].

The mass of chromium adsorbed by sand at breakpoint increases as the initial concentration of chromium increased. Cr(III) mass removed by one gram of sand was 0.0614 mg/g and 1.39 mg/g for the initial concentrations 4.95 ppm and 206 ppm, respectively. This can be explained by the fact that as the concentration of Cr(III) ions increases so does the metal ion loading on the adsorbent. For example, a concentration of 206 ppm will have higher surface loading as compared to concentration of 4.95 ppm and the volume of 206 ppm Cr(III) solution treated less than for 4.95 ppm Cr(III) solution. However when the influent concentration will be higher more number of ions will be competing for the same adsorption sites and will go through without being adsorbed. Plot of uptake of mass of Cr(III) per grams of sand versus the initial concentration of Cr(III) at breakpoint is shown in figure [13]. The increase of metal uptake by sand by changing the initial concentration of Cr(III) may attribute to the cooperative binding at sand sited upon

adsorption of chromium. The results of the percentage removal of Cr(III) agree with those of Baig study [121] which showed that the percentage increased with decreasing influent initial concentration, but the results are small compared to Baig results. This difference is due to the depth and internal diameter of sand column which is bigger in Baig study and the flow rate is less, and this increased the percentage removal of Cr(III) from aqueous solution [121].

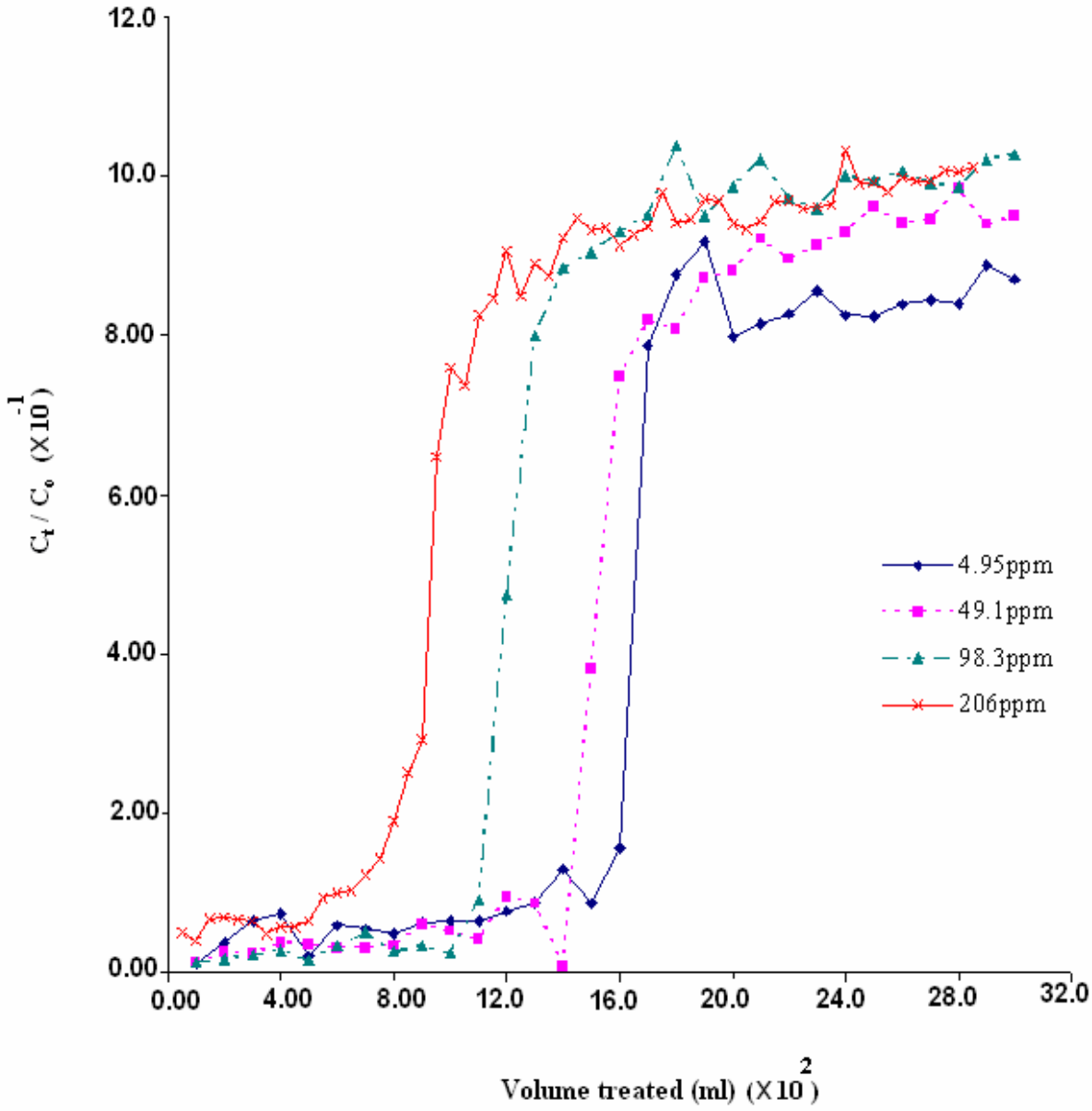

Figure (12A), Breakthrough curves of removal of Cr(III), by sand at different initial concentrations at room temperature and pH 1.00. The flow rate was 6.0 ml/min, sand size 18-mesh, sand weight 120.0 g and sand depth 19.0 cm.

C_t: concentration of Cr(III) treatment with time

C_o: initial concentration of Cr(III)

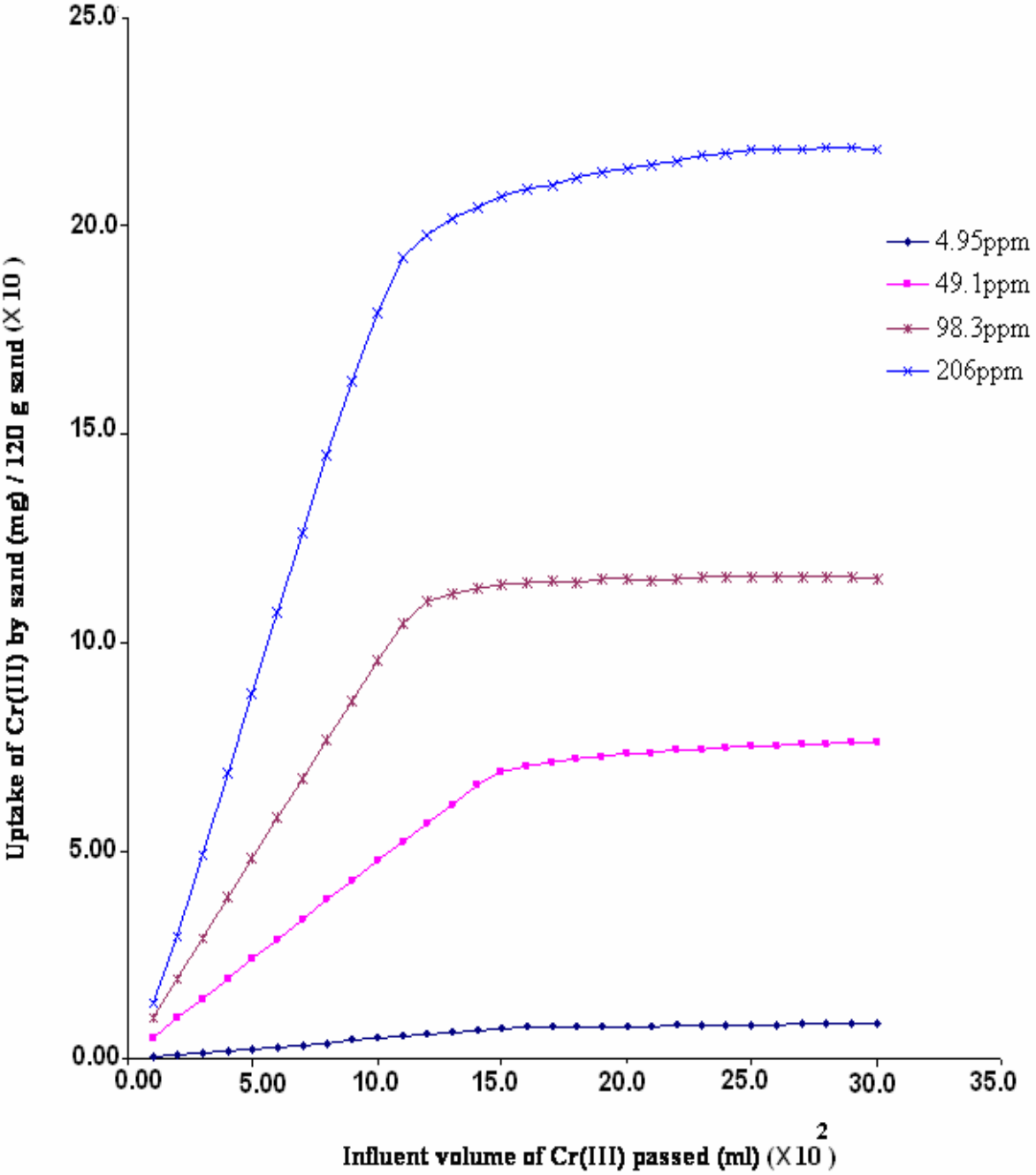

Figure [12B], Uptake of Cr(III) by sand by passing 3000 ml of different concentration of Cr(III) solution at room temperature and pH 1.00. The flow rate was 6.0 ml/min, sand size 18-mesh, sand weight 120.0 g and sand depth 19.0 cm.

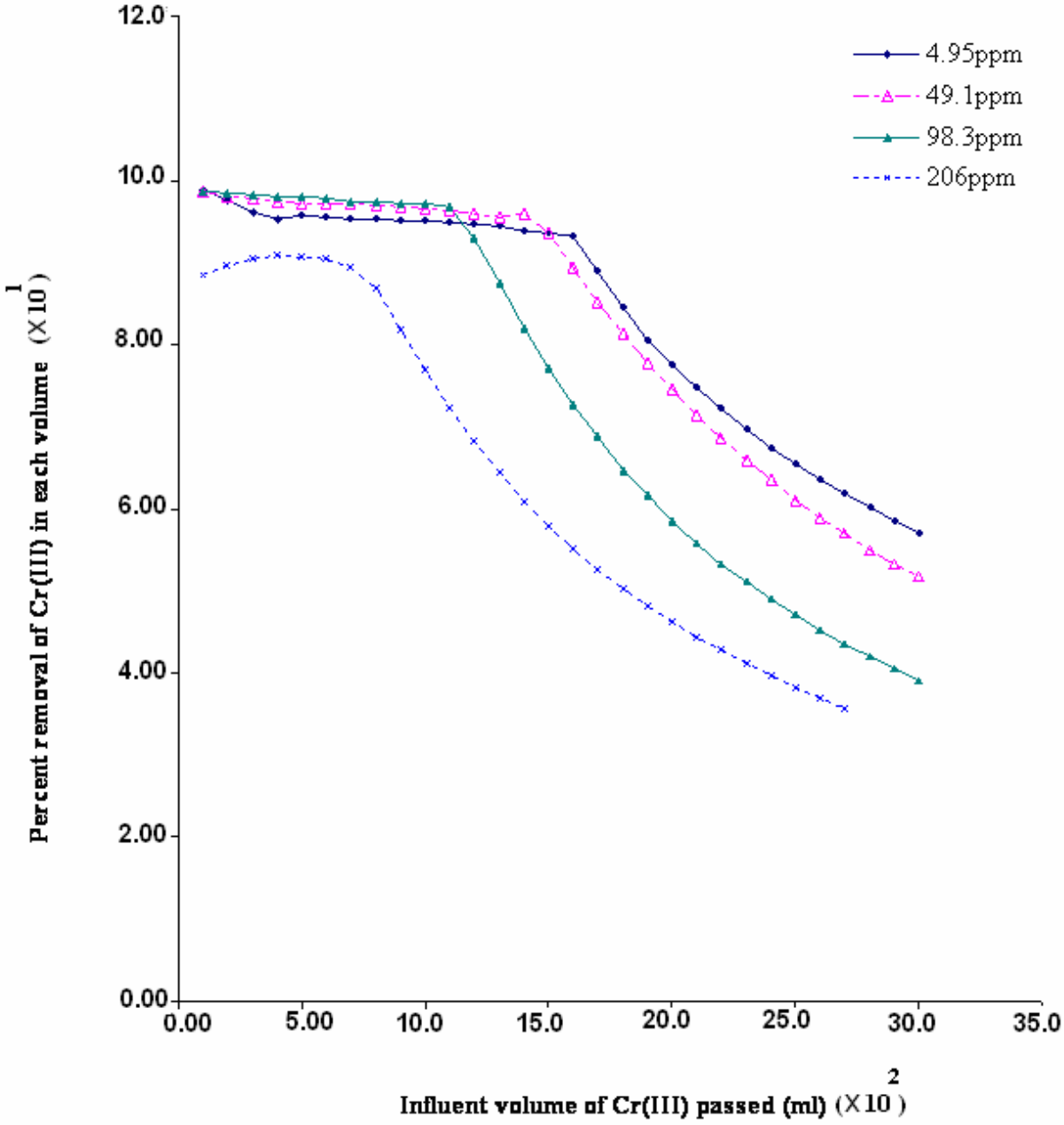

Figure [12C], Percent removal Cr(III) by sand by passing 3000 ml of different concentration of Cr(III) solution at room temperature, and pH 1.00. The flow rate was 6.0 ml/min, sand size 18-mesh, sand weight 120.0 g and sand depth 19.0cm.

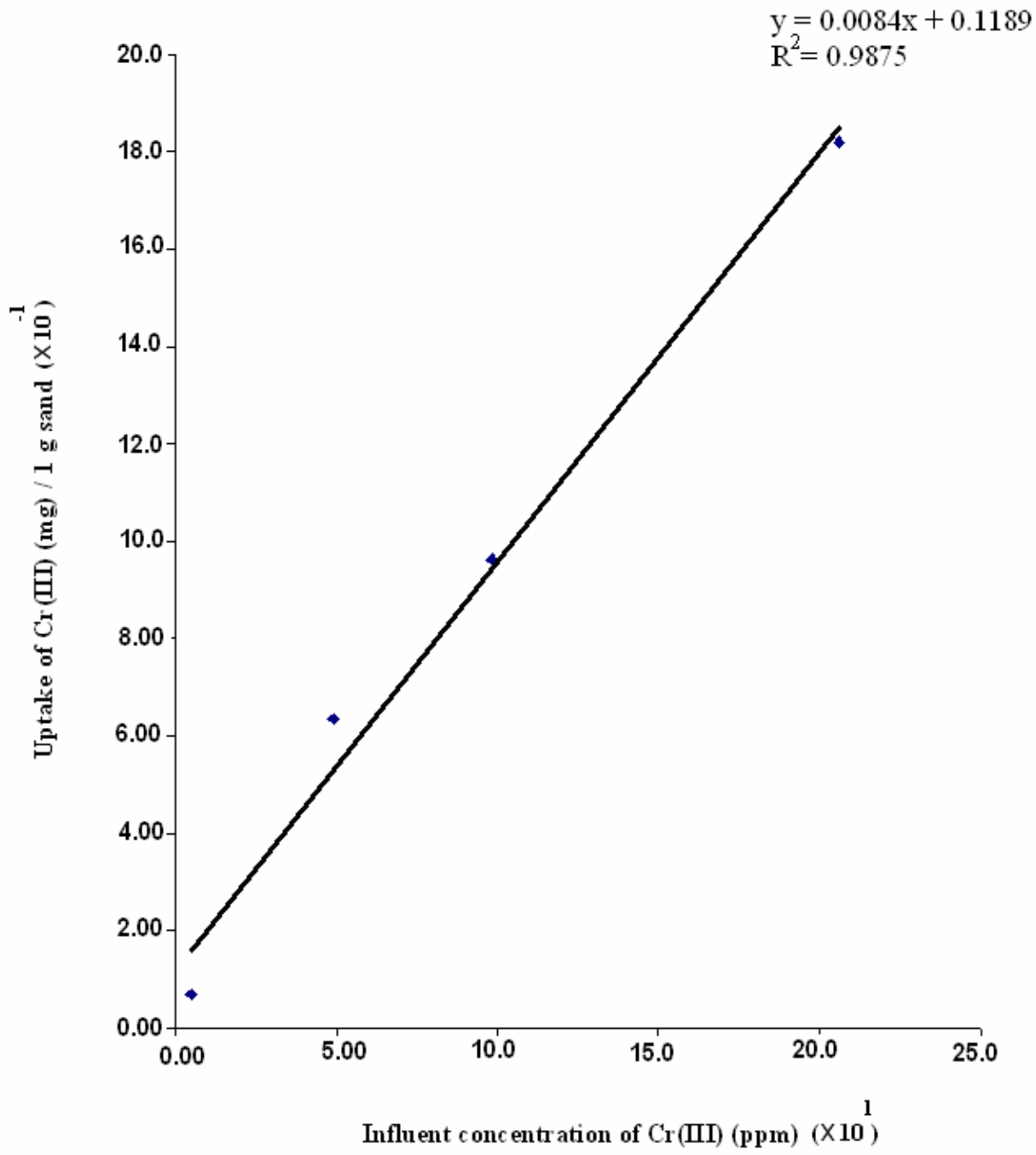

Figure [13], Mass of Cr(III) uptake by sand by passing 3000 ml of different concentration of Cr(III) solution at room temperature and pH 1.00. The flow rate was 6.0 ml/min, sand size 18-mesh, sand weight 120.0 g and sand depth 19.0 cm.

III.3.2. Effect of sand column on the pH of effluent solution

In solution, trivalent chromium is affected by pH. At low pH, Cr(III) is found as Cr^{+3} and at neutral and high pH it exists in the form $Cr(OH)_3$. The removal of Cr(III) by sand column was performed at pH 1. Stock solutions of Cr(III) in buffer was subjected to the column. The monitoring of the effluent pH during the adsorption process showed a significant increasing of pH that measured for the influent and effluent solution passed through sand columns table [10]. The pH can affect both the adsorbent (sand) and the form of Cr(III). At very acidic medium silicate ions are formed in buffer and create a buffering capacity. This does not exist at higher pH values. On the other hand, the pH affecting the chromium exists where at pH 1 $CrCl_3$ is predominant, and at higher pH $Cr(OH)_3$ is formed and precipitated inside the column. . It was found that the pH of the effluent solution was higher than the pH of the influent one. The difference was greater for lower pH and become less for increasing pH until pH 8. Most chromium removal from the column by continuous elution at buffer solution happened at pH 1, and no chromium eluted at pH 2, 3, 4, 5, and 6, table [1]. This can be argued to the presence of Cr(III) in the form of $CrCl_3$.

Removal of Cr(III) by sand column at pH 4 and 10 was 92% and 98% respectively, which showed no significant effect of the metal initial concentration on the removal efficiency of Cr(III) from aqueous solution, for the concentrations 50-250 ppm [(121)]. The percentage removal reached 93.1% when treating 1600 ml of 4.95 ppm solution and 90.2% when treating 900 ml of 206 ppm by continuous flow of influent solution for both concentrations [(121)]. It's obvious that two mechanism work. The first occurs at very acidic pH in which Cr(III) is adsorbed by sand. At alkaline pH, Cr(III) is mostly precipitated inside the column as $Cr(OH)_3$.

Table [10], Change of pH of the influent by passing through the sand column.

pH_i (influent solution)	pH_f (effluent solution)
0.97	4.52
2.03	4.87
2.98	4.93
4.03	4.94
4.99	5.40
5. 95	6.05
7.03	7.12
7.95	7.96

III .3.3. Effect of column depth

The effect of column depth on the adsorption of 62.3 ppm Cr(III) using Three sequential columns (three plates and the length of three plates was 57.0 cm) and one column (one plate and the length of plate was 19.0 cm) packed with 18-mesh sand at room temperature and pH 1.00 was studied and the data presented in table [11]. 100 ml of 62.3 ppm Cr(III) was passed through the columns then the columns are eluted by 1000 ml of buffer pH 1. A grab sample after every 100 ml of buffer solution eluted is analyzed to measure chromium content. Constant flow rate, 2.30 ml/min, was achieved by adjusting the tap of the columns. The percentage removal of chromium for three plates was 100% and 93.1% for one plate but the mass of Cr(III) (mg) uptake by one gram sand was 0.017 for three plates and 0.048 for one plate which is three times bigger than for three plates. But the 100% removal chromium is expected for more plates.

Table [11], Effect of column bed depth on the percentage removal of Cr(III) by sand loaded with 6.23 mg of Cr(VI). The elution volume was 1000 at room temperature and pH 1. The flow rate was 2.30 ml/min, and sand 18-mesh.

Depth of column	57.0 cm (360.0 g of sand)	19.0 cm (120.0 g of sand)
Percent removal of Cr(III) by sand	100	93.1
Mass of Cr(III) (mg) uptake by sand	6.23	5.80

III.4. Potential of speciation

Speciation of chromium has attracted a great deal of interest in view of the toxic properties of Cr(VI) compared with the much less toxic of Cr(III).Wool was found to be a good selective adsorbent for Cr(VI) and did not adsorb Cr(III) from their aqueous solution at low pH by batch adsorption. The optimum results obtained at pH 2, and contact time two hours [(40)]. The results obtained from continuous adsorption agreed with those of batch one. The wool is highly efficient for selective Cr(VI) removal at pH 1. Wool was able to remove 97.0% out of three liters of solution containing 208 ppm of Cr(VI) and the percentage removal of Cr(VI) should reach 100% if we use three successive columns since the bed depth is increased. It is clear that pH determines the speciation of the Cr(VI) as will as providing a favorable adsorbent surface charge for the adsorption to occur. The advantage of continuous adsorption over batch is the stability of pH due to the solution flow through the column and consequently preventing local increase of pH results by OH^- release from wool.

The three sequential columns (three plates) packed with wool or sand was studied trying to reach 100% percentage removal for Cr(VI) and Cr(III) by wool and sand respectively. The results of wool columns showed that two additions of 100 ml of 48.6 ppm Cr(VI) to wool columns and then eluted with one liter of buffer solution pH 1; that the percent removal of Cr(VI) by wool increased from 84.3% in first addition to 88.3% in the second addition . And the results of sand columns showed that four additions of 100 ml of 62.3 ppm Cr(III) to sand columns and then eluted with one liter of buffer solution pH 1.00; that the percent removal of Cr(III) by sand decreased from 100% in first addition to 51.1% in the fourth , tables [12 and 13]. The results obtained suggested that wool is selective for Cr(VI) adsorption and not for Cr(III) from their aqueous solution at low pH in previous work (batch technique) and also in the continuous flow technique [(40)]. Accordingly, successive columns can be used to partially speciate Cr(VI) and Cr(III) with more than 85% efficiency; that is wool at low pH does not adsorb Cr(III) and adsorb Cr(VI), so the mixture of both ions could pass in sequence through column packed with wool and then through column packed with sand.

Table [12], Removal of Cr(VI) by wool by adding two times* of 100 ml of 48.6 ppm Cr(VI) then eluted with 1000 ml of buffer pH 1.00 after each time through three sequential columns packed with wool at room temperature. The flow rate was 2.30 ml/min, and wool fiber length 0.50 cm, wool weight 78.0 g and wool depth 57.0 cm.

Number of additions of Cr(VI)	Percent removal of Cr(VI) by wool (%)	Uptake of Cr(VI) (mg) by wool	Uptake of Cr(VI) (mg) / 1g wool
1	84.3	4.09	0.0524
2	88.3	7.91	0.101

* In the three wool columns after two additions we stopped adding more, since the results of addling seven additions for one column (section III.2.6), showed maximum percent removal ~ 77%.

Table [13], Removal of Cr(III) by sand by adding four times of 100 ml of 62.3 ppm Cr(III) then eluted with 1000 ml of buffer pH 1.00 after each time through three sequential columns packed with sand at room temperature. The flow rate was 2.30 ml/min, and sand 18-mesh, weight 360.0 g and 57.0 cm depth.

Number of additions of Cr(III)	Percent removal of Cr(III) by sand	Uptake of Cr(III) (mg) by sand	Uptake of Cr(III) (mg) / 1 g sand
1	100	6.23	0.0173
2	100	12.5	0.0347
3	94.9	17.7	0.0492
4	51.1	12.7	0.0353

IV. Conclusion

The experimental results showed that wool and sand can remove chromium ions effectively from its solution at low pH through continuous flow method. Wool selectively removes Cr(VI) at pH 1 and sand is very effective in removing Cr(III) and some of Cr(VI) at pH 1 .

The percentage removal of Cr(VI) by wool increased with increased Cr(VI) initial concentration. At relatively high concentration of Cr(IV), 208 ppm, the percentage removal of chromium reached 97.0%. Dyeing wool with Acid Alizarin Violet, an acid dye, didn't affect the percentage of Cr(VI) removal, and consequently the dye didn't occupy the binding sites on which chromium is adsorbed.

Two mechanisms are believed to exist when Cr(VI) is bind to wool. The first is irreversible binding to some wool functional groups, physi-sorption, and the second is binding to reversible sites. Since two phenomena were taking place on the surface of the wool: (1) the adsorption of the chromium on the active sites and (2) the desorption of the chromium, leaching. The desorption is found dependent on temperature and contact time between the mobile phase, Cr(VI) buffered solution, and wool. The amount of Cr(VI) desorbed from wool is leached from the Cr(VI) bound to the reversible wool binding sites. The positive value of the enthalpy $\Delta H°$, the positive value of entropy $\Delta S°$, and the negative values of free energy $\Delta G°$ indicates that the desorption process is endothermic and spontaneous.

The advantage of continuous adsorption over the none continuous (batch) is the stability of pH due to the solution flow through the column and consequently preventing local increase of pH resulting from OH^- release from wool. In other words, the chemical and structural forms of wool in the continuous flow column are very different from that of wool in batch adsorption. This consequently may result in variable mechanisms of interaction with the metal ion in both techniques.

Sand is found to be very effective in removing Cr(III) from its solution even at relatively high concentration at 206 ppm, the percentage removal of chromium reached 90.2%. The percentage removal increased with decreasing the initial concentration of Cr(III). The removal efficiency increases with the depth of the sand column. It was found that the pH of the effluent solution was higher than the pH of the influent one. The difference was greater for lower pH. This becomes less upon increasing pH until pH 8.

V

REMOVAL OF CHROMIUM BY DUCKWEED

V. 1. Removal of chromium by Duckweed

Duckweed is among the smallest and simplest freshwater floating plants. They grow under a variety of climatic conditions in most parts of the world; also they can tolerate a wide pH range, but grows best at pH values from 4.5 to 7.5, figure [14]. The plant can grow in full sunlight as well as in dense shade. Duckweed growth rate is optimum at 20-30 °C. The plant biomass is rich in protein (20-35% of dry weight) and vitamins. Duckweed could also be specifically applied as bio-accumulators for heavy metals. All members of the duckweed family concentrate heavy metals in particular cadmium, chromium and lead, which may at times reach levels in the plant which are harmful to both the health and growth of the plant [84, 124-26].

Many reports are available on the uptake of metal ions by duckweeds and the numerous interactions that occur. Duckweeds will uptake and concentrate Cd, N, Cr, Zn, Sr, Co, Fe, Mn, Cu, Pb, Al and even Au. To attempt to define the rates of accumulation is not important here, except to point out that as the levels of these elements rise to higher than normal in general they may directly inhibit growth of the plant and any animal those consume significant quantities. At low level accumulation the plants become a very useful source of trace minerals particularly for livestock and fish [84, 125, 126].

Duckweed exposed to 10 ppm of Zn, Pb and Ni for 96 hours and it was found that duckweed accumulated 27, 10, and 5.5 µg /mg of Zn, Pb and Ni respectively [84]. The amount of chlorophyll was decreased in Duckweed due to the accumulation and toxicity of heavy metals as Pb, Zn, Ni and Cd. It has been suggested that heavy metals disrupt the membrane system, leading to the breakdown of permeability barrier which leads to the efflux of cations [83, 84, 128].

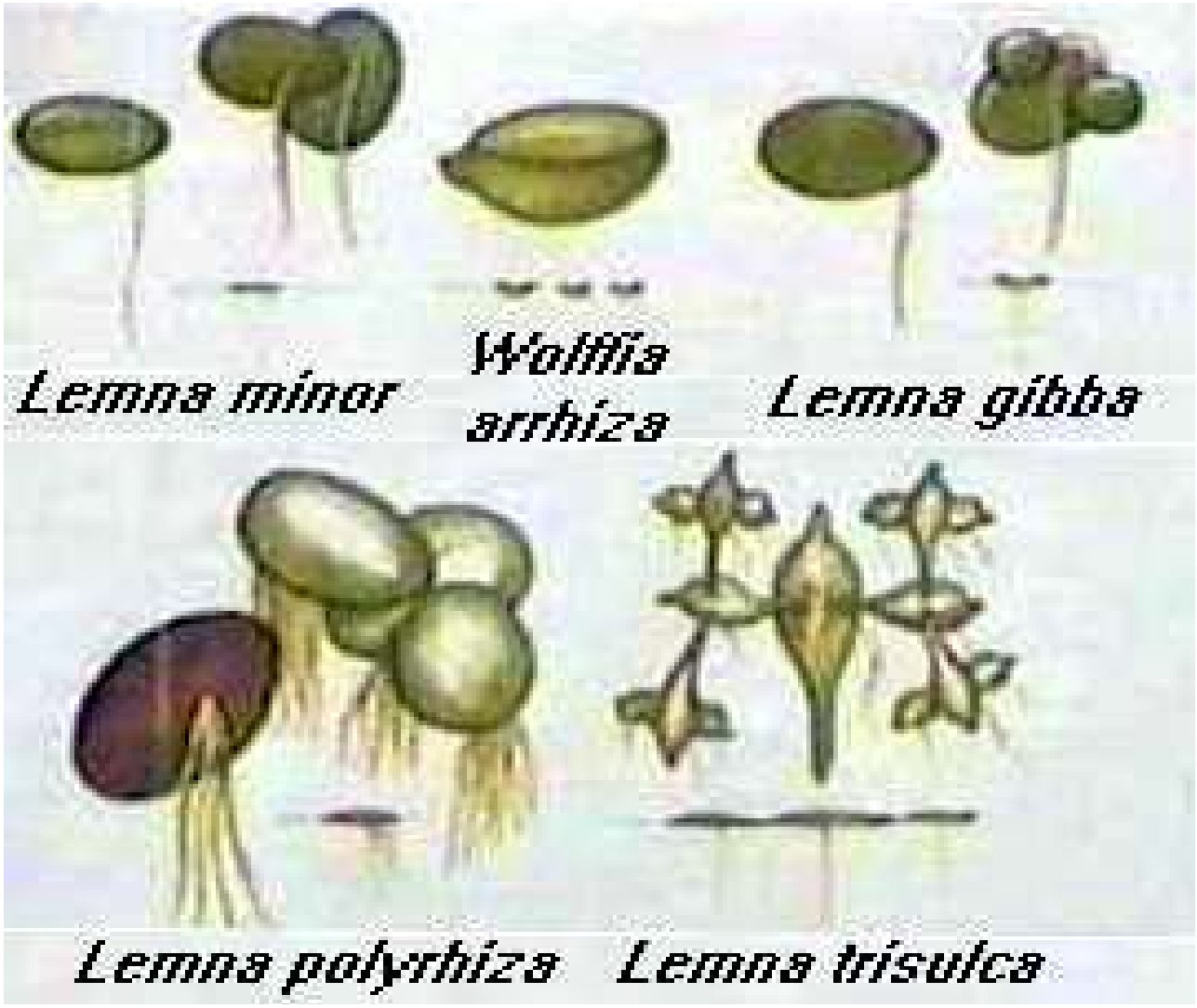

Figure [14], The various duckweeds species

The accumulation of heavy metals by duckweed is not normally a problem for those wishing to use duckweeds from natural water resources or effluent from human or intensive animal housing as these metals are normally at extremely low concentrations. Duckweeds, however, are contaminated by such heavy metals from industries such as tanning (chromium) leached from mining (e.g. cadmium) and great care is needed where water is contaminated to be sure that heavy metals do not get into the human food chain. On the other hand, duckweeds may find use in stripping heavy metals from industrial water. Also their content of heavy metals can be used to indicate potential pollution levels of waters [125-128].

Duckweed accumulated Cr(III) and Cr(VI) and the accumulation increased as the corresponding chromium ion concentration increased from 5 to 20 ppm in solution contain copper and zinc at pH 6. The results of analysis showed that the remainder chromium metal ion species in solution that were not accumulated by duckweed were richer in Cr(III) than in Cr(VI) regardless of the initial concentration of total Cr, Cu^{+2} and Zn^{+2} [127].

Duckweed plants were collected from wastewater pond from Al-Aroub Agricultural station and rinsed with deionized water. This plant used to study the accumulation of chromium by the duckweed at different temperatures. 10.0 grams of duckweed (wet weight) were rinsed with distilled water, and then placed in one liter plastic beaker containing 600 ml nutrient solution with or without test metal and partially covered to prevent evaporation [26]. Three replicates were considered for all treatment in this experiment. After 24.0 hours the data were analyzed using Atomic Absorption Spectroscopy and presented in table [14]. It was found that the percentage removal of chromium is very small and the duckweed was dead as expected due to the accumulation of heavy metal. Also final pH and electric conductivity of the sample solution were measured and found a bit than initial one. It is obvious that the percentage removal of Cr(VI) increased with increasing the temperature until 28 ºC but with time increasing the percentage removal seems not change. The percentage removal was calculated by the equation (5):

$$\text{Percentage removal of Cr(VI)} = ((C_c - C_d)/ C_c)*100\ \% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where,

C_c the concentration of Cr(VI) in control beaker

C_d the concentration of Cr(VI) in duckweed beaker

Table [14], Percent removal of Cr(VI) by Duckweed by adding 10.0 g of fresh Duckweed to the one liter solution contains 7.0 ppm of Cr(VI) and nutrition at three different temperatures 23, 25 and 28 °C.

Time of treatment (hour)	Percentage removal of Cr(VI) by Duckweed at 23 ºC (%)	Percentage removal of Cr(VI) by Duckweed at 25 ºC (%)	Percentage removal of Cr(VI) by Duckweed at 28 ºC (%)
0.50	2.71	8.25	14.0
2.0	3.94	8.01	14.5
4.0	2.00	7.87	13.6
6.0	0.53	8.09	15.3
24	5.72	7.30	14.2

It was found that increasing the time of treatment to 48.0 hours that slightly increases in the percentage removal of Cr(VI) by Duckweed which causes death to this plant. This result agreed with the results obtained by other studies [84, 125]. Figure [15] and table [15] show the results obtained. The experiments were stopped due to that the conditions of the experiments were not fixed, duckweed was dead and also the duckweed was contaminated with heavy metals and this was proved by analyzing the wastewater of the duckweed ponds in Al-Aroub station.

Table [15], Percentage removal of Cr(VI) by Duckweed by adding 10.0 g of fresh Duckweed to the one liter solution contains 7.0 ppm of Cr(VI) and nutrition at 25 °C.

Time of treatment (hour)	Concentration of Cr(VI) in Control beaker (ppm)	Concentration of Cr(VI) in duckweed beaker (ppm)	Percent removal of Cr(VI) by duckweed (%)
0.50	7.68	7.09	7.66
2.0	6.29	6.06	3.68
4.0	5.42	5.03	7.24
6.0	4.89	4.53	7.41
8.0	6.92	6.43	7.01
22	6.93	6.21	10.4
24	6.56	6.08	7.34
28	6.34	5.85	7.62
30	6.19	5.60	9.59
46	5.80	5.16	10.9
48	7.20	6.47	10.1

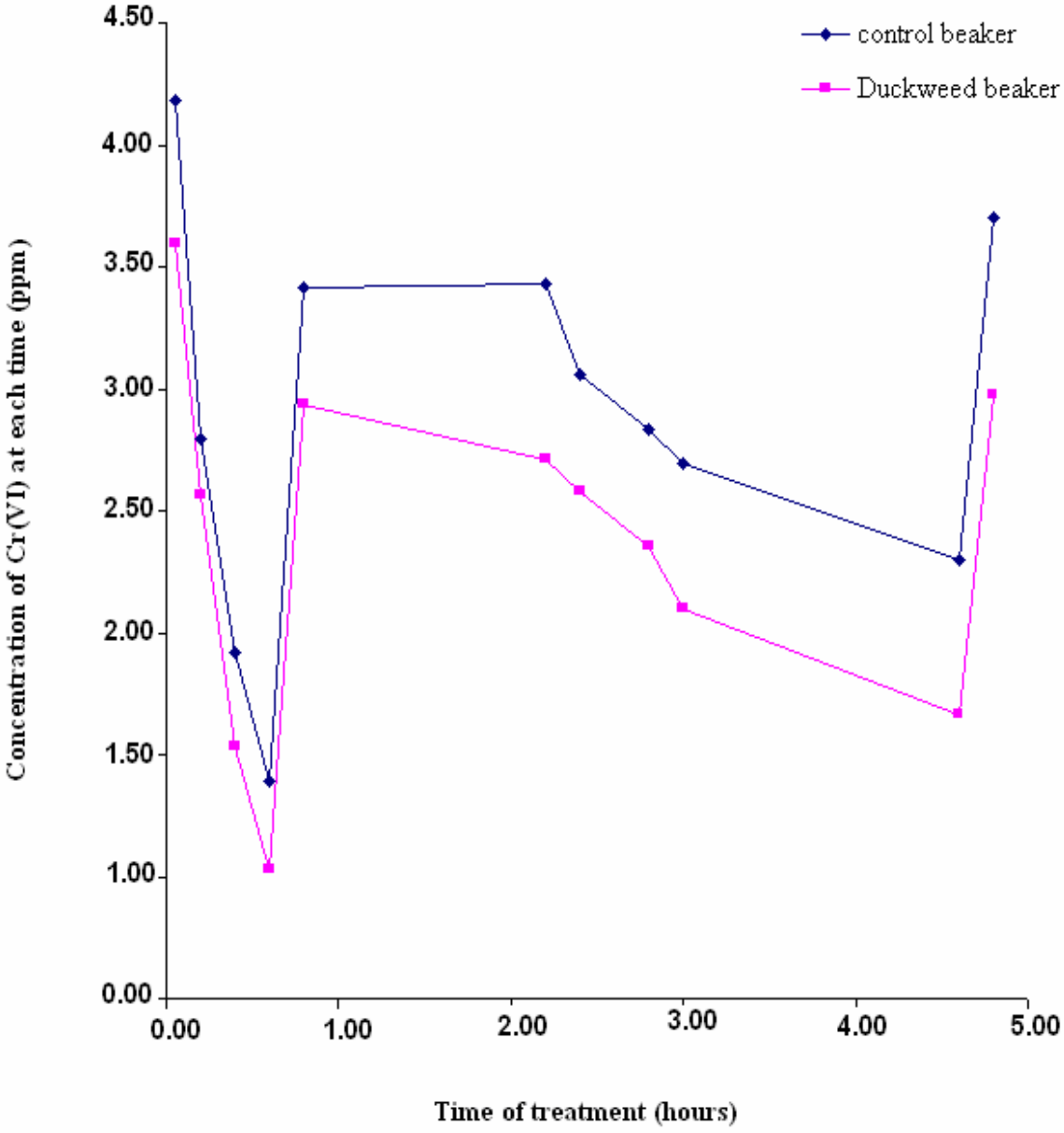

Figure [15], Percent removal of Cr(VI) by Duckweed by adding 10.0 g of fresh Duckweed to one liter solution contains 7.0 ppm of Cr(VI) and nutrition (Duckweed beaker) and other one liter solution contain 7 ppm of Cr(VI) and nutrition (control beaker) at 25 °C.

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